Supplementray Information for

Stereocontrolled Synthesis of Quaternary Cyclopropyl Esters

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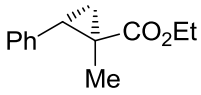
General Conditions

Commercially available reagents were used as received without further purification. All reactions required anhydrous conditions and were conducted in flame-dried apparatus under an atmosphere of nitrogen. Reactions in DME at 130 ºC were conducted in 10 ml thick walled microwave vials (CEM) fitted with crimp top teflon seals. Analytical thin-layer chromatography (TLC) was performed on silica gel plates (0.25mm) precoated with a fluorescent indicator. Standard flash chromatography procedures were performed using Kieselgel 60 (40-63 μm) or with a Varian Superflash automated purification system. Petrol refers to the fraction boiling between 40-60 ºC. Residual solvent was removed using a static oil pump (< 1 mbar). Optical rotations were recorded on a Jasco P1010 polarimeter. Infrared spectra were recorded directly as neat liquids on a Bruker Tensor 37 FTIR machine fitted with a PIKE MIRacle ATR accessory. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ at 400 and 100 respectively on Bruker AV400 or AMX400 machines. Chemical shifts are reported relative to $CHCl_3$ [δ_H 7.27] and $CDCl_3$ [δ_C 77.0]. Mass spectra were obtained by the EPSRC National Mass Service (Swansea) using a high resolution double focussing mass spectrometer **(**Finnigan MAT 95 XP).

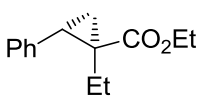
Reaction Procedures and Compound Data

(1*R*,2*S*)-Ethyl 1-Methyl-2-phenyl-cyclopropanecarboxylate[1] 1a



To a solution of triethyl 2-phosphonopropionate (0.42 ml, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-Styrene oxide (114 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the title compound **1a** (195 mg, 95%) as colourless oil: $[\alpha]_D$ −142.0 (*c* 1.7, Me_2CO); IR (cm^{-1}) 1714, 1603, 1499 , 1454 , 1381, 1311, 1240, 1206, 1151, 1112, 1078, 1060, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.08 (m, 5H, 5 × ArH), 4.10 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.73 (dd, *J* = 9.2 and 7.0 Hz, 1H, CH), 1.61 (dd, *J* = 9.2 and 4.5 Hz, 1H, 1 of cyclopropane-CH_2), 1.21 (t, *J* = 7.1 Hz, 3H, CH_2*Me*), 1.08 (dd, *J* = 7.0 and 4.5 Hz, 1H, 1 of cyclopropane-CH_2), 0.91 (s, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 137.0, 129.3, 128.1, 126.6, 60.7, 31.6, 25.1, 19.9, 14.5, 14.2; HRMS *m/z* (M + H^+, 100%) Found: 205.1223 $C_{13}H_{17}O_2$ requires 205.1223.

(1*R*,2*S*)-Ethyl 1-ethyl-2-phenylcyclopropanecarboxylate[1] 1b

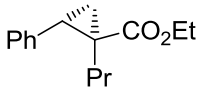


To a solution of triethyl 2-phosphobutyrate (0.48 ml, 2.00 mmol) in DME (4.0 ml) at 25°C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-Styrene oxide (114 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was

(1) Panne, P.; DeAngelis, A.; Fox, J. M. *Org. Lett.* **2008**, 10, 2987-2989.

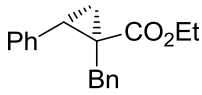
removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the title compound **1b** (211 mg, 97%) as colourless oil: $[\alpha]_D$ –107.8 (*c* 1.07, Me_2CO); IR (cm^{-1}): 1715, 1606, 1582, 1500, 1451, 1393, 1379, 1319, 1302, 1275, 1209, 1152, 1105, 1085, 1050, 1028; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.09 (m, 5H, 5 × ArH), 4.18-4.04 (m, 2H, OCH_2), 2.73 (dd, *J* = 9.2 and 7.0 Hz, 1H, CH), 1.61-1.51 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H, OCH_2*Me*), 1.08 (dd, *J* = 7.0 and 4.5 Hz, 1H, 1 of cyclopropane-CH_2), 0.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 137.1, 129.3, 128.1, 126.6, 60.6, 32.3, 31.4, 21.8, 17.8, 14.3, 11.7; HRMS *m/z* (M + H^+, 100%) Found: 219.1380 $C_{14}H_{19}O_2$ requires 219.1380.

(1*R*,2*S*)-Ethyl 2-phenyl-1-propylcyclopropanecarboxylate 1c



To a solution of triethyl 2-phosphonopentanoate (533 mg, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-Styrene oxide (114 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1c** (216 mg, 93%) as colourless oil: $[\alpha]_D$ –113.6 (*c* 1.41, Me_2CO); IR (cm^{-1}): 1713, 1603, 1498, 1453, 1381, 1291, 1224, 1205, 1151, 1071, 1025; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.09 (m, 5H, 5 × ArH), 4.17-4.04 (m, 2H, OCH_2), 2.67 (dd, *J* = 9.6 and 7.2 Hz, 1H, cyclopropane-CH), 1.61 (ddd, *J* = 9.2, 4.5 and 1.1 Hz, 1H, 1 of CH_2), 1.57-1.48 (m, 1H, 1 of CH_2), 1.34-1.18 (m, 2H, CH_2), 1.21 (t, *J* = 7.4 Hz, 3H, OCH_2*Me*), 1.10 (dd, *J* = 7.2 and 4.5 Hz, 1H, 1 of cyclopropane-CH_2), 0.76-0.68 (1H, m, 1 of cyclopropane-CH_2), 0.66 (3H, t, *J* = 7.4, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 137.1, 129.2, 128.1, 126.6, 60.6, 32.0, 30.6, 30.4, 20.7, 17.9, 14.2, 14.2; HRMS *m/z* (M + H^+, 100%) Found: 233.1538 $C_{15}H_{21}O_2$ requires 233.1536.

(1*S*,2*S*)-Ethyl 1-benzyl-2-phenylcyclopropanecarboxylate 1d

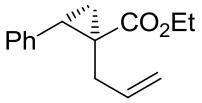


To a solution of 2-benzyltriethylphosphonoacetate[2] (629 mg, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-Styrene oxide (114 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1d** (275 mg, 98%) as colourless oil: $[\alpha]_D$ +16.5 (*c* 1.09, Me_2CO); IR (cm^{-1}): 1714, 1603, 1583, 1496, 1453, 1380, 1301, 1194, 1135, 1095, 1078, 1053, 1027; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.14 (m, 5H, 5 × ArH), 4.24-4.08 (m, 2H, OCH_2), 3.23 (d, *J* = 15.4 Hz, 1H, 1 of $PhCH_2$), 2.89 (dd, *J* = 9.1 and 7.0 Hz, 1H, cyclopropane-CH), 2.03 (d, *J* = 15.4 Hz, 1H, 1 of $PhCH_2$), 1.93 (dd, *J* = 9.1 and 4.8 Hz, 1H, 1 of cyclopropane-CH_2), 1.45 (dd, *J* = 4.8 and 3.9 Hz, 1H, 1 of cyclopropane-

(2) Lehnert, W. *Tetrahedron* **1974**, *30*, 4723-4724.

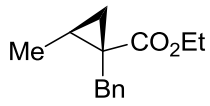
CH_2), 1.21 (t, *J* = 7.1 Hz, 3H, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 140.4, 136.7, 129.3, 128.7, 128.4, 128.0, 127.0, 125.9, 60.9, 33.5, 32.7, 30.9, 17.9, 14.1; HRMS *m/z* (M + H^+, 100%) Found: 281.1532 $C_{19}H_{21}O_2$ requires 281.1536.

(1*R*,2*S*)-Ethyl 1-allyl-2-phenylcyclopropanecarboxylate 1e



To a solution of 2-allyl triethylphosphonoacetate[3] (529 mg, 2.00 mmol) in DME (4.0 ml) at 25 °C was added n-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-Styrene oxide (114 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1e** (198 mg, 86%) as colourless oil: $[\alpha]_D$ –65.0 (*c* 1.86, Me_2CO); IR (cm^{-1}): 2981; 1716, 1641, 1499, 1431, 1382, 1304, 1219, 1203, 1151, 1079, 1027; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10 (m, 5H, 5 × ArH), 5.75-5.63 (m, 1H, =CH), 4.85-4.74 (m, 2H, $=CH_2$), 4.17-4.04 (m, 2H, OCH_2), 2.77 (t, *J* = 9.0 Hz, 1H, cyclopropane-CH), 2.36 (ddd, *J* = 15.4, 6.1 and 1.2 Hz, 1H, 1 of allylic-CH_2), 1.65 (ddd, *J* = 9.0, 4.5 and 0.9 Hz, 1H, 1 of cyclopropane-CH_2), 1.49 (dd, *J* = 15.4 and 10.4 Hz, 1H, 1 of allylic-CH_2), 1.21 (t, *J* = 7.1, 3H, Me), 1.16 (dd, *J* = 7.3 and 4.5 Hz, 1H, 1 of cyclopropane-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 136.7, 135.9, 129.3, 128.2, 126.8, 115.7, 60.7, 32.5, 32.0, 29.5, 17.7, 14.2. HRMS m/*z* (M + H^+, 100%) Found: 231.1382 $C_{15}H_{19}O_2$ requires 231.1380.

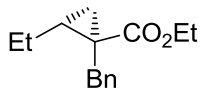
(1*R*,2*S*)-Ethyl 1-benzyl-2-methylcyclopropanecarboxylate 1f



To a solution of 2-benzyltriethylphosphonoacetate[2] (629 mg, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*R*)-Propylene oxide (70 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1f** (172 mg, 79%) as colourless oil: $[\alpha]_D$ +10.1 (*c* 0.61, Me_2CO); IR (cm^{-1}): 1716, 1605, 1498, 1455, 1382, 1303, 1195, 1137, 1097, 1079, 1029; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.08 (m, 5H, 5 × ArH), 4.01-3.84 (m, 2H, OCH_2), 3.14 (d, *J* = 15.1 Hz, 1H, 1 of $PhCH_2$), 2.71 (d, *J* = 15.1 Hz, 1H, 1 of $PhCH_2$), 1.60-1.51 (m, 1H, CH), 1.43 (dd, *J* = 9.1 and 4.1 Hz, 1H, 1 of CH_2), 1.13 (d, *J* = 6.3 Hz, 3H, Me), 1.04 (t, *J* = 7.1 Hz, 3H, OCH_2*Me*), 0.48 (dd, *J* = 6.6 and 4.1 Hz, 1H, 1 of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 140.7, 128.5, 128.1, 125.8, 60.5, 33.3, 27.8, 22.3, 21.9, 14.1, 14.1; HRMS *m/z* (M + H^+, 100%) Found: 219.1377 $C_{14}H_{19}O_2$ requires 219.1380.

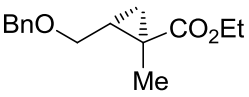
(3) Minami, T.; Hirakawa, K.; Koyanagi, S.; Nakamura, S.; Yamaguchi, M. *J. Chem. Soc., Perkin Trans. 1*. **1990**, 2385-2390.

(1*S*,2*R*)-Ethyl 1-benzyl-2-ethylcyclopropanecarboxylate 1g



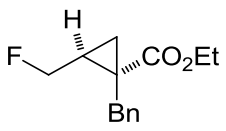
To a solution of 2-benzyltriethylphosphonoacetate[2] (629 mg, 2.00 mmol) in DME (4.0 ml) at 25°C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*S*)-1,2-Epoxybutane (87 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1g** (177 mg, 76%) as colourless oil: $[\alpha]_D$ –3.24 (*c* 0.5, Me_2CO); IR (cm^{-1}): 1730, 1666, 1600, 1511, 1493, 1453, 1377, 1261, 1229, 1208, 1178, 1156, 1074, 1029; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20-7.05 (m, 5H, 5 × ArH), 4.01-3.90 (m, 2H, OCH_2), 3.25 (d, *J* = 15.3 Hz, 1H, 1 of $PhCH_2$), 2.59 (d, *J* = 15.3 Hz, 1H, 1 of $PhCH_2$), 1.55-1.36 (m, 3H), 1.35-1.25 (m, 1H, 1 of Me*CH*$_2$), 1.04 (t, *J* = 7.1 Hz, 3H, *Me*CH_2), 0.96 (t, *J* = 7.2 Hz, 3H, OCH_2*Me*), 0.52-0.48 (m, 1H, 1 of cyclopropane-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 140.8, 128.6, 128.1, 125.8, 60.5, 33.4, 29.8, 28.1, 22.8, 21.0, 14.1, 13.9; HRMS *m/z* (M + H^+, 100%) Found: 233.1534 $C_{15}H_{21}O_2$ requires 233.1536.

(1*R*,2*R*)-Ethyl 2-(benzyloxymethyl)-1-methylcyclopropanecarboxylate 1h



To a solution of triethyl 2-phosphonopropionate (0.42 ml, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*R*)-Benzyl glycidyl ether (153 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20 ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the title compound **1h** (194 mg, 78%) as colourless oil: $[\alpha]_D$ +60.6 (*c* 1.74, Me_2CO); IR (cm^{-1}): 1717, 1498, 1456, 1369, 1347, 1323, 1308, 1279, 1178, 1153, 1078, 1030; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 5H, 5 × ArH), 4.53 (q, *J* = 11.9 Hz, 2H, O*CH*$_2$Me), 4.18-4.03 (m, 2H, O*CH*$_2$CH), 3.66 (dd, *J* = 10.6 and 5.8 Hz, 1H, 1 of $PhCH_2$), 3.37 (dd, *J* = 10.6 and 8.5 Hz, 1H, 1 of $PhCH_2$), 1.86 (tt, *J* = 8.6 and 6.2 Hz 1H, $BnOCH_2CH$), 1.40 (dd, *J* = 9.3 and 4.2 Hz, 1H, 1 of cyclopropane-*CH*$_2$), 1.31 (s, 1H, Me), 1.24 (t, *J* = 7.1 Hz, 3H, OCH_2*Me*), 0.54 (dd, *J* = 6.3 and 4.3 Hz, 1H, 1 of cyclopropane-*CH*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 138.2, 128.4, 127.7, 127.6, 72.8, 69.3, 60.6, 25.7, 22.7, 20.4, 14.1, 13.9; HRMS *m/z* (M + H^+, 100%) Found: 249.1485 $C_{15}H_{21}O_3$ requires 249.1485.

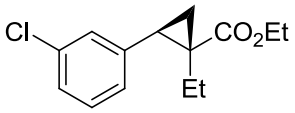
(1*R,2*S**)-Ethyl 1-benzyl-2-(fluoromethyl)cyclopropanecarboxylate 1i**



To a solution of 2-benzyltriethylphosphonoacetate[2] (629 mg, 2.00 mmol) in DME (4.0 ml) at 25°C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. Epifluorohydrin (71 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and

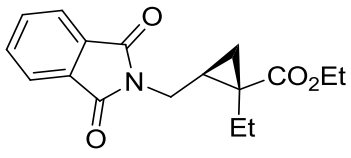
filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1i** (177 mg, 75%) as colourless oil: IR (cm^{-1}) 1718, 1605, 1497, 1454, 1412, 1369, 1305, 1247, 1206, 1170, 1136, 1096, 1080, 1055; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.07 (m, 5H, 5 × ArH), 4.61 (ddd, *J* = 48.0, 10.4 and 5.7 Hz, 1H, 1 of FCH_2), 4.32 (ddd, *J* = 48.0, 10.4 and 9.0 Hz, 1H, 1 of FCH_2), 4.07-3.94 (m, 2H, OCH_2), 3.30 (d, *J* = 15.9, 1H, 1 of Ph*CH*$_2$), 2.75 (d, *J* = 15.9, 1H, 1 of Ph*CH*$_2$), 2.03-1.93 (m, 1H, CH), 1.58-1.51 (m, 1H, 1 of cyclopropane-CH_2), 1.06 (t, *J* = 7.1 Hz, 3H, Me), 0.84-0.76 (m, 1H, 1 of cyclopropane-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 139.8, 128.5, 128.2, 126.1, 82.7 (d, *J* = 16.4 Hz), 61.0, 33.3, 28.4 (d, *J* = 3.4) 26.1 (d, *J* = 24.2), 18.1 (d, *J* = 8.8), 14.0; HRMS *m/z* (M + H^+, 100%) Found: 254.1553 $C_{14}H_{18}FO_2$ requires 254.1551.

(1*S*,2*R*)-Ethyl 2-(3-chlorophenyl)-1-ethylcyclopropanecarboxylate 1j



To a solution of triethyl 2-phosphonobutyrate (0.48 ml, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*R*)-3-Chlorostyrene oxide (127 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1j** (185 mg, 73%) as colourless oil: $[\alpha]_D$ +99.0 (*c* 1.39, Me_2CO); IR (cm^{-1}) 1716, 1598, 1377, 1313, 1241, 1154, 1060; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 3H, 3 × ArH), 7.17-7.08 (m, 1H, 1 × ArH), 4.28-4.15 (m, 2H, OCH_2), 2.80 (dd, *J* = 8.7 and 7.2 Hz, 1H, ArCH), 1.71-1.61 (m, 2H, *CH*$_2$CH$_3$), 1.32 (t, *J* = 7.1 Hz, 3H, OCH_2*Me*), 1.16 (dd, *J* = 7.0 and 1.8 Hz, 1H, 1 of CH_2), 0.98-0.86 (m, 4H, Me and 1 of CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 139.3, 134.0, 129.3, 129.3, 127.5, 126.8, 60.7, 31.7, 31.5, 21.8, 17.9, 14.2, 11.7; HRMS *m/z* (M + H^+, 100%) Found: 253.0986 $C_{14}H_{18}{}^{35}ClO_2$ requires 253.0990.

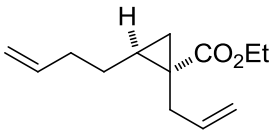
(1*S*,2*S*)-Ethyl 2-((1,3-dioxoisoindolin-2-yl)methyl)-1-ethylcyclopropanecarboxylate 1k



To a solution of triethyl 2-phosphonobutyrate (0.48 ml, 2.00 mmol) in DME (1.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (*R*)-*N*-(2,3-epoxypropyl)phthalamide (203 mg, 1.00 mmol) was dissolved in DME (3.0 ml) and transferred drop wise into the phosphonate via cannula. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (10% EtOAc/petrol) to give the *title compound* **1k** (172 mg, 57%) as colourless oil: $[\alpha]_D$ +22.6 (*c* 0.85, Me_2CO); IR (cm^{-1}) 1774, 1708, 1616. 1468, 1435, 1389, 1368, 1329, 1305, 1246, 1158, 1115, 1089, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.4, 3.0 Hz, 2H, 2 × ArH), 7.65 (dd, *J* = 5.4 and 3.0 Hz, 2H, 2 × ArH), 4.01 (q, *J* = 7.2 Hz, 2H, OCH_2), 3.90 (dd, *J* = 14.1 and 5.8 Hz, 1H, 1 of NCH_2), 3.50 (dd, *J* = 14.1 and 9.2 Hz, 1H, 1 of NCH_2), 1.92-1.82 (m,

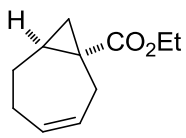
1H, 1 of CH_2CH_3), 1.81-1.72 (m, 1H, 1 of CH_2CH_3), 1.69-1.59 (m, 1H, CH), 1.25 (dd, *J* = 9.2 and 4.4 Hz, 1H, 1 of cyclopropane-CH_2), 1.14 (t, *J* = 7.2 Hz, 3H, OCH_2Me), 1.00 (t, *J* = 7.3 Hz, 3H, Me), 0.65 (dd, *J* = 6.5 and 4.4 Hz, 1H, 1 of cyclopropane-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 168.2, 134.0, 132.1, 123.3, 60.6, 37.5, 29.4, 25.4, 22.0, 19.7, 14.2, 12.5; HRMS *m/z* (M + H^+, 100%) Found: 302.1390 $C_{17}H_{20}NO_4$ requires 302.1387.

(1*S,2*S**)Ethyl 1-allyl-2-(but-3-enyl)cyclopropanecarboxylate 1l**



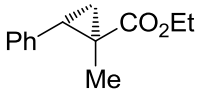
To a solution of 2-allyl triethylphosphonoacetate[4] (529 mg, 2.00 mmol) in DME (4.0 ml) at 25 °C was added *n*-butyllithium (2.5 M; 0.82 ml, 2.05 mmol) dropwise over 5 min. (±)-1,2-Epoxy-5-hexene (113 μl, 1.00 mmol) was added in one portion. The reaction was heated to 130 °C for 20 h. The reaction was cooled before sat. aq. NH_4Cl (8 ml) was added. The reaction was extracted three times with Et_2O (3 × 20 ml). The organic layers were combined, dried over $MgSO_4$ and filtered before the solvent was removed *in vacuo*. The residue was loaded onto 5 ml of silica and purified by flash column chromatography (4% EtOAc/petrol) to give the *title compound* **1l** (179 mg, 86%) as colourless oil: IR (cm^{-1}) 3079; 2981; 2929, 1718, 1641, 1435, 1399, 1367.0, 1307, 1209, 1157, 1043; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91-5.69 (m, 2H, 2 × =CH), 5.02-4.85 (m, 4H, 2 × =CH_2), 4.03 (qd, *J* = 7.1, 1.7 Hz, 2H, OCH_2), 2.48 (dd, *J* = 15.4, 6.2 Hz, 1H, 1 of allylic-CH_2), 2.15-2.03 (m, 3H, 3 of allylic-CH), 1.62-1.50 (m, 1H, 1 of alkyl-CH_2), 1.47-1.37 (1H, m, cyclopropane-CH), 1.36-1.27 (m, 2H, 1 of cyclopropane-CH_2 and 1 of alkyl-CH_2), 1.16 (t, *J* = 7.1 Hz, 3H, Me), 0.36 (dd, *J* = 6.7, 4.1 Hz, 1H, 1 of cyclopropane-CH_2); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.2, 138.1, 136.6, 115.6, 114.9, 61.6, 60.5, 33.7, 32.7, 28.6, 27.2, 26.9, 20.8, 14.0; HRMS *m/z* (M + H^+, 100%) Found: 209.1530 $C_{13}H_{21}O_2$ requires 209.1536.

Ethyl bicyclo[5.1.0]oct-3-ene-1-carboxylate 2



To a solution of ethyl 1-allyl-2-(but-3-enyl)cyclopropanecarboxylate **1l** (392 mg, 1.59 mmol) in CH_2Cl_2 (15.0 ml) at 25 °C was added Grubb's 1st generation catalyst (5 mol%, 66 mg, 0.08 mmol) in one portion. The reaction was heated to 40 °C for 12 h. The reaction was cooled and the residue was loaded onto 5 ml of silica and purified by flash column chromatography (100% petrol) to give the *title compound* **2** (161 mg, 56%) as colourless oil: IR (cm^{-1}) 2930, 2856, 1715, 1447, 1367, 1305, 1194, 1153, 1037; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67-5.57 (m, 1H, =CH), 5.42-5.34 (m, 1H, =CH), 4.02 (q, *J* = 7.1 Hz, 2H, OCH_2), 2.79 (dd, *J* = 16.2, 8.1 Hz, 1H, 1 of allylic-CH_2), 2.28-2.20 (m, 2H, alkyl-CH_2) 1.99 (m, 2H, 2 of allylic-CH_2), 1.59-1.46 (m, 2H, 1 of allylic-CH_2 and cyclopropane-CH), 1.32 (dd, *J* = 7.9 and 3.9, 1H, 1 of cyclopropane-CH_2), 1.15 (t, *J* = 7.1 Hz, 3H, Me), 0.67 (dd, *J* = 5.1 and 3.8 Hz, 1H, 1 of cyclopropane-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 129.6, 127.1, 60.4, 30.9, 30.9, 28.0, 27.9, 26.2, 24.7, 14.2; HRMS *m/z* (M + H^+, 100%) Found: 181.1230 $C_{11}H_{17}O_2$ requires 181.1229.

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



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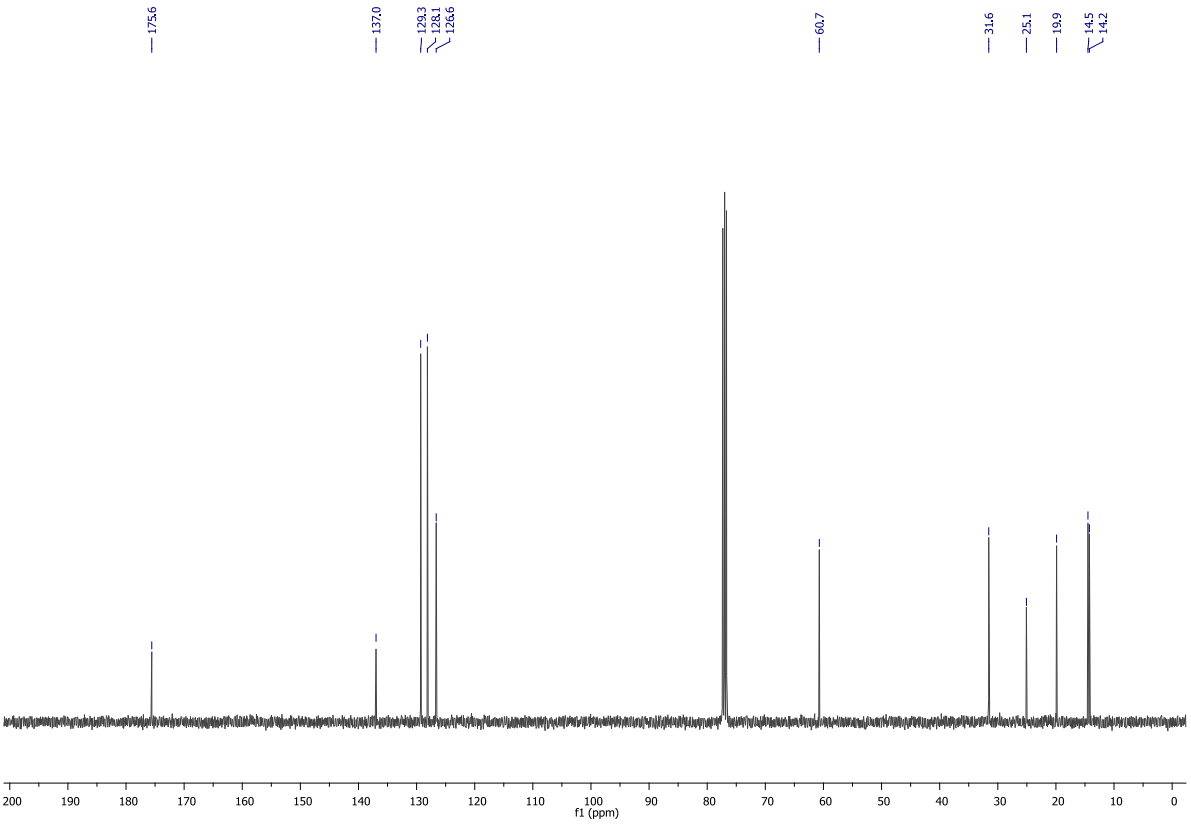

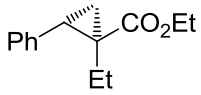

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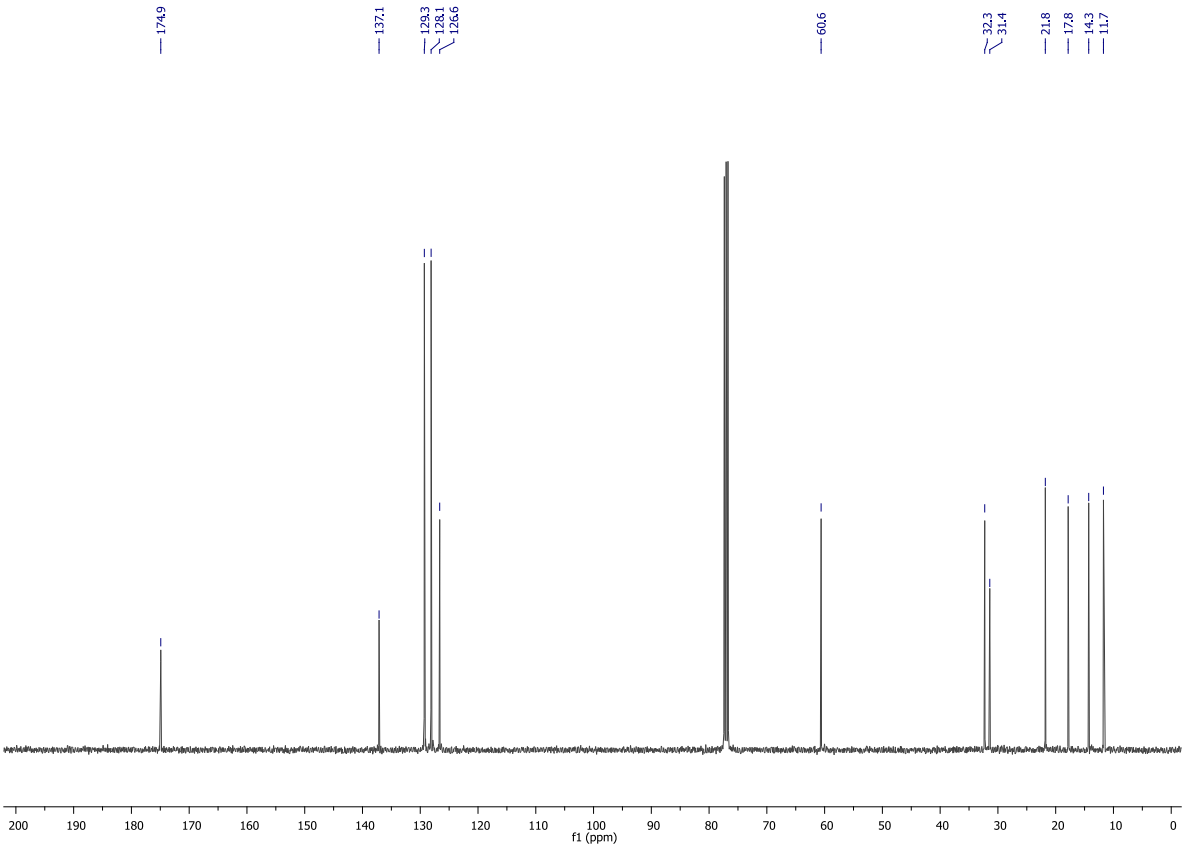

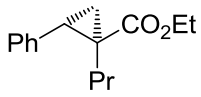

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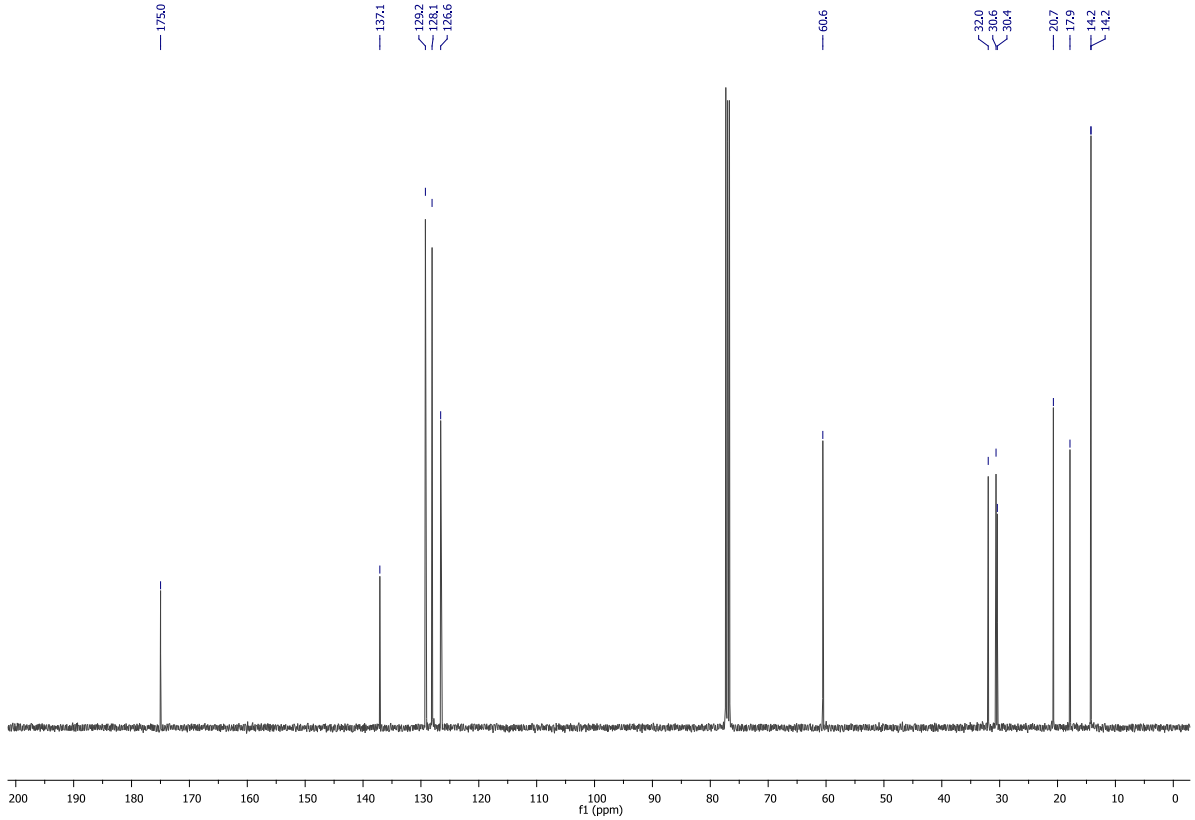

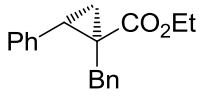

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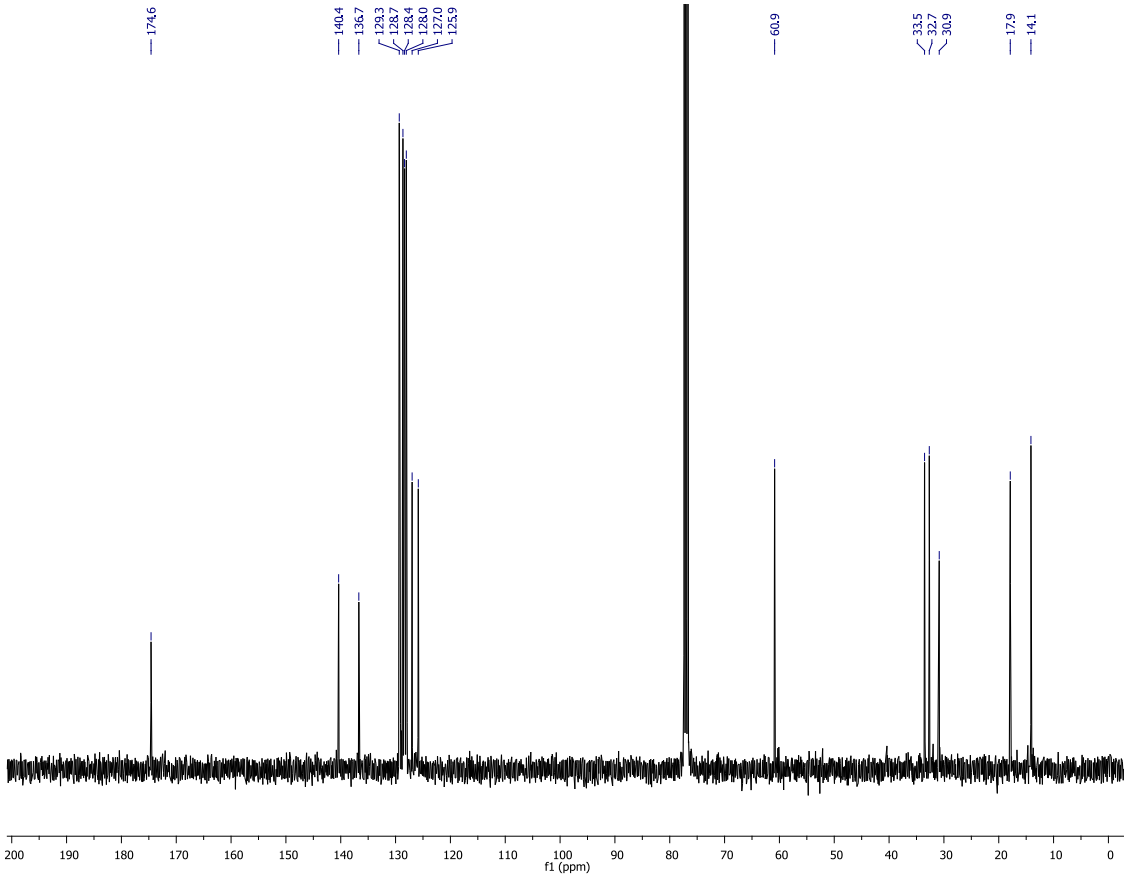

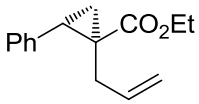

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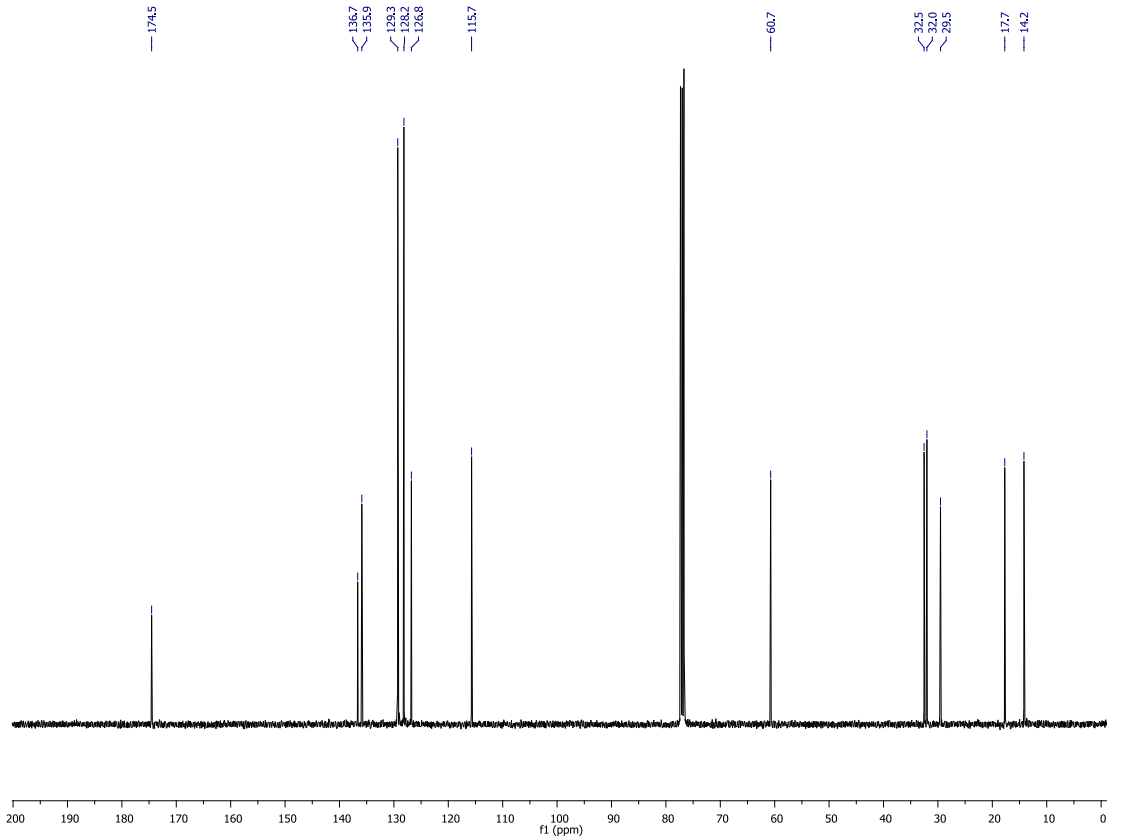

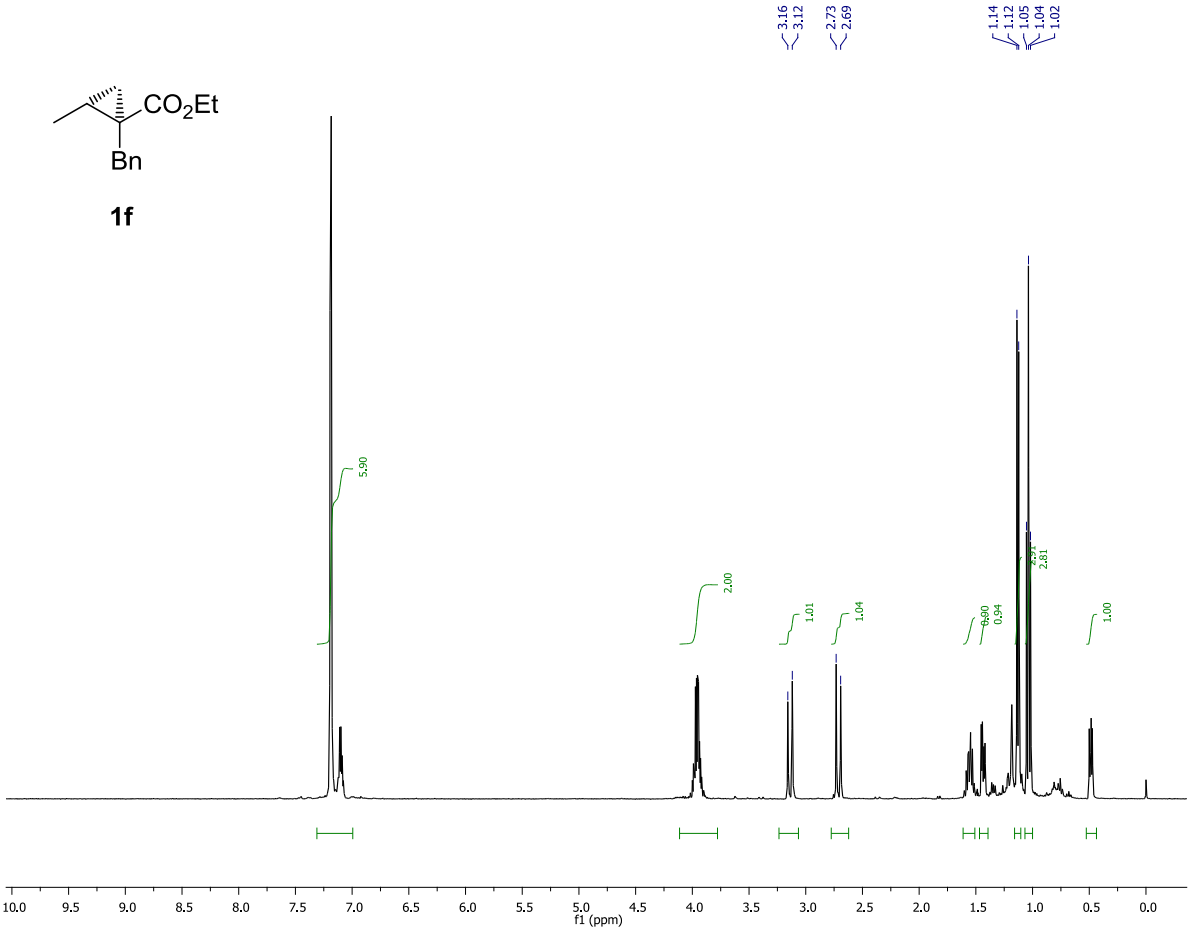

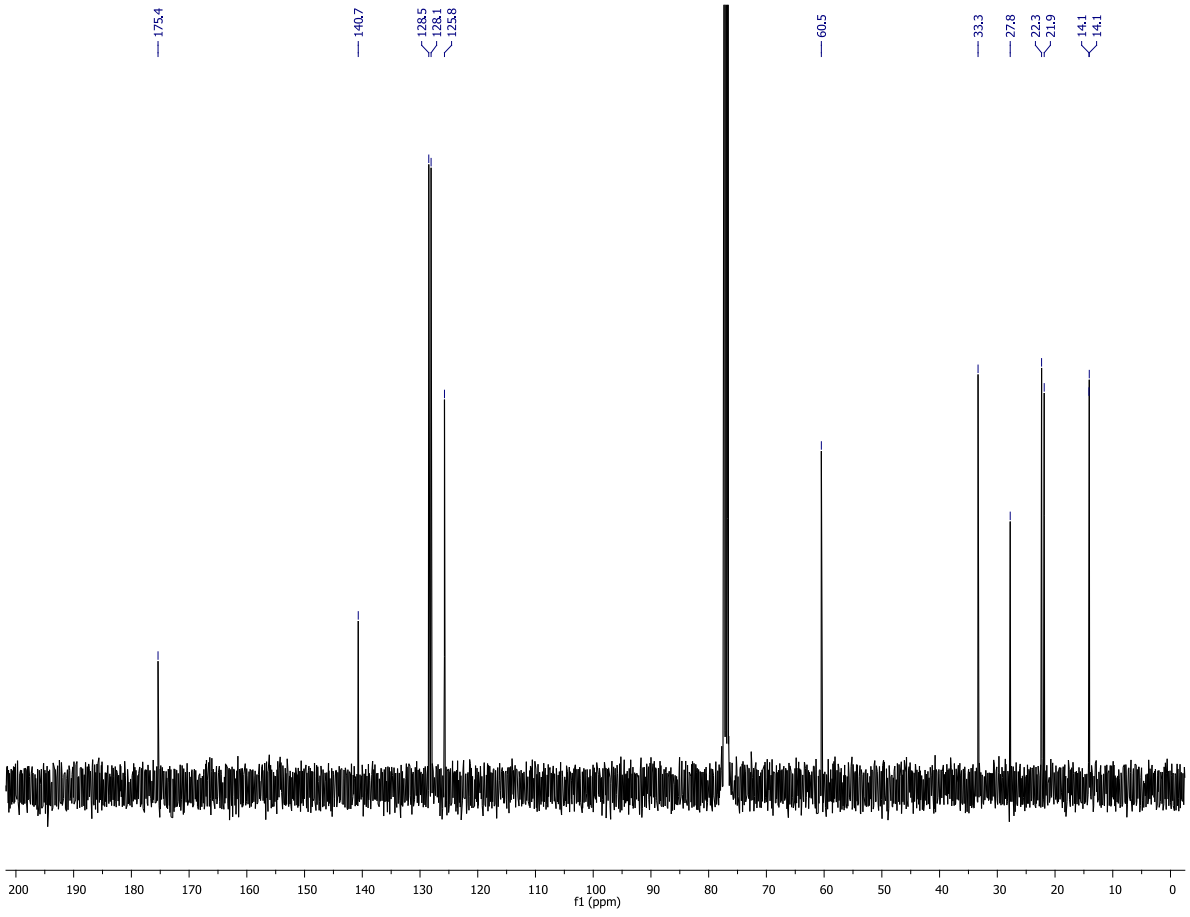

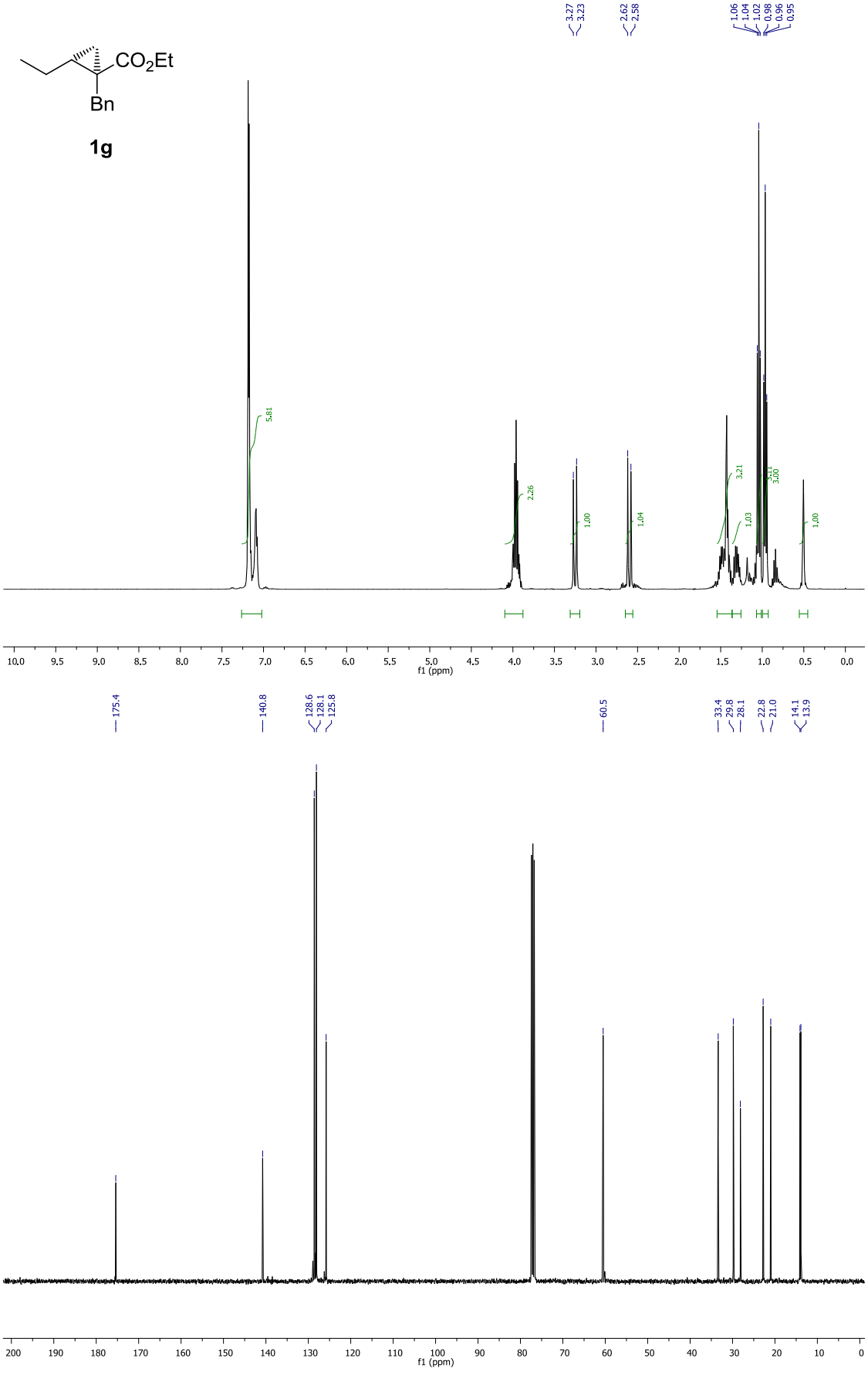

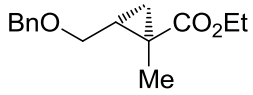
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CO2Et
Me

1h

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3.67
3.66
3.64
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3.37
3.37
3.35
1.42
1.41
1.40
1.39
1.31
1.26
1.24
1.22
0.56
0.55
0.54
0.53
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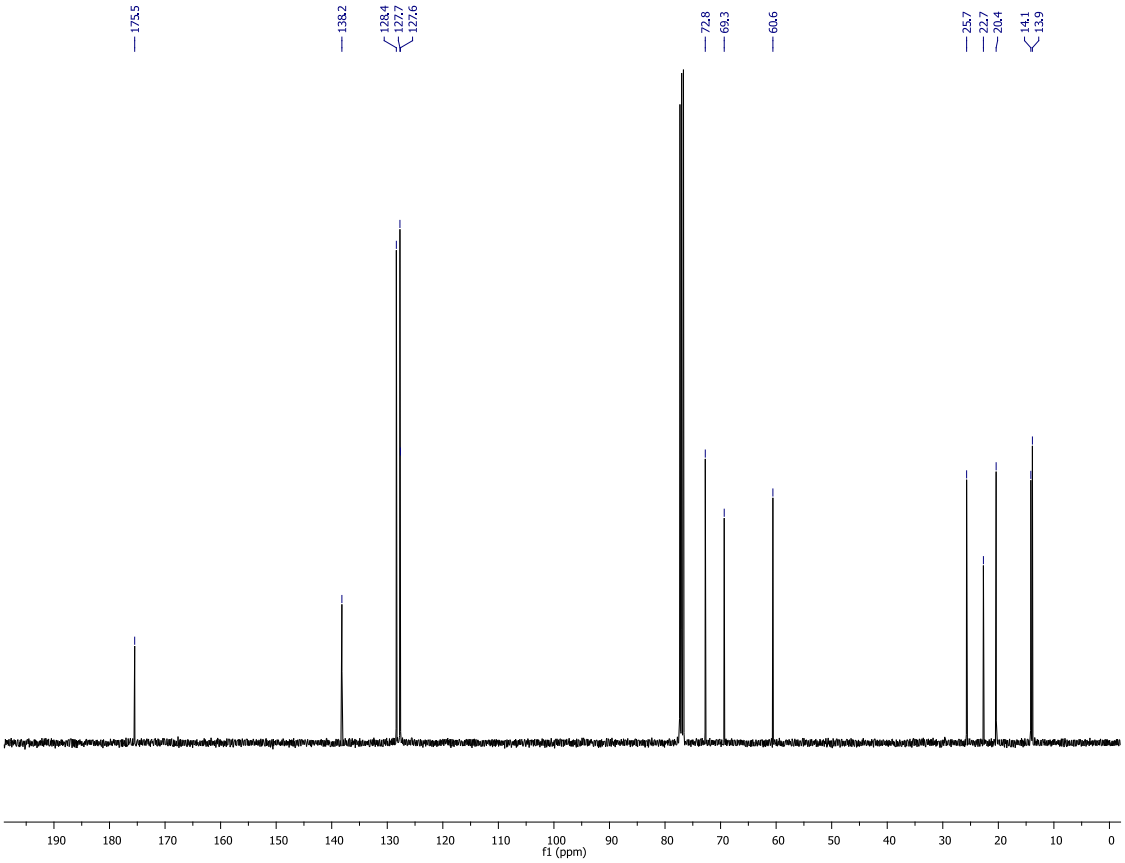
2.08
1.03
1.00
0.99
3.12
3.50
1.00
f1 (ppm)


175.5
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127.7
127.6
72.8
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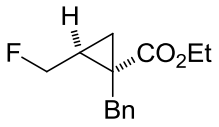
60.6
25.7
22.7
20.4
14.1
13.9
f1 (ppm)



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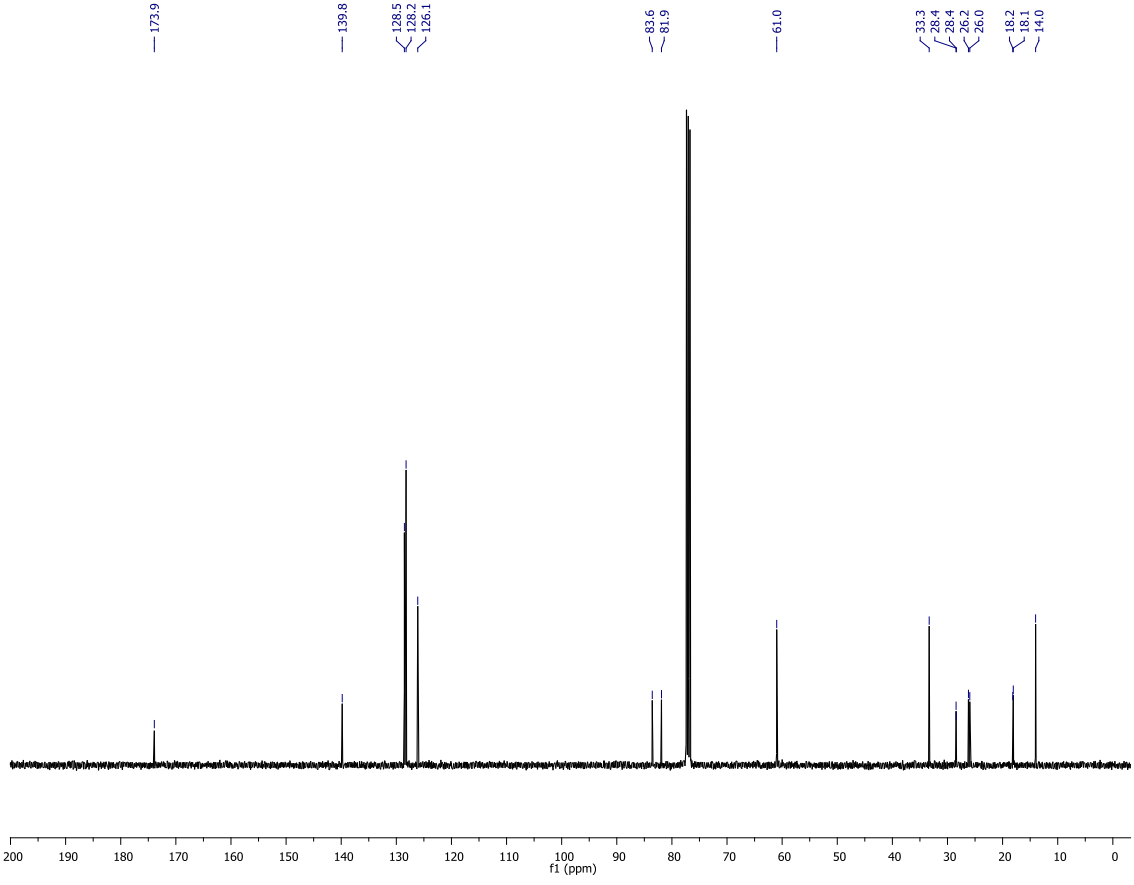

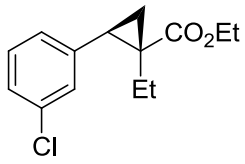

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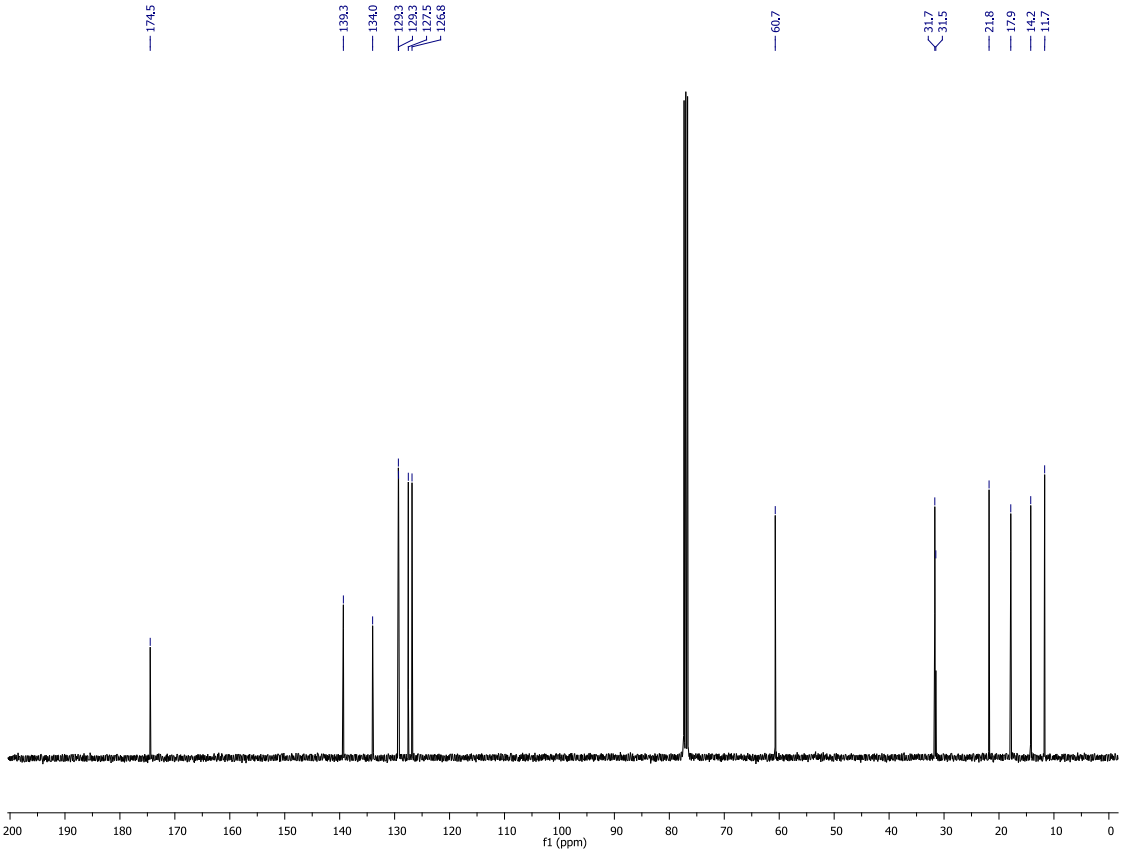

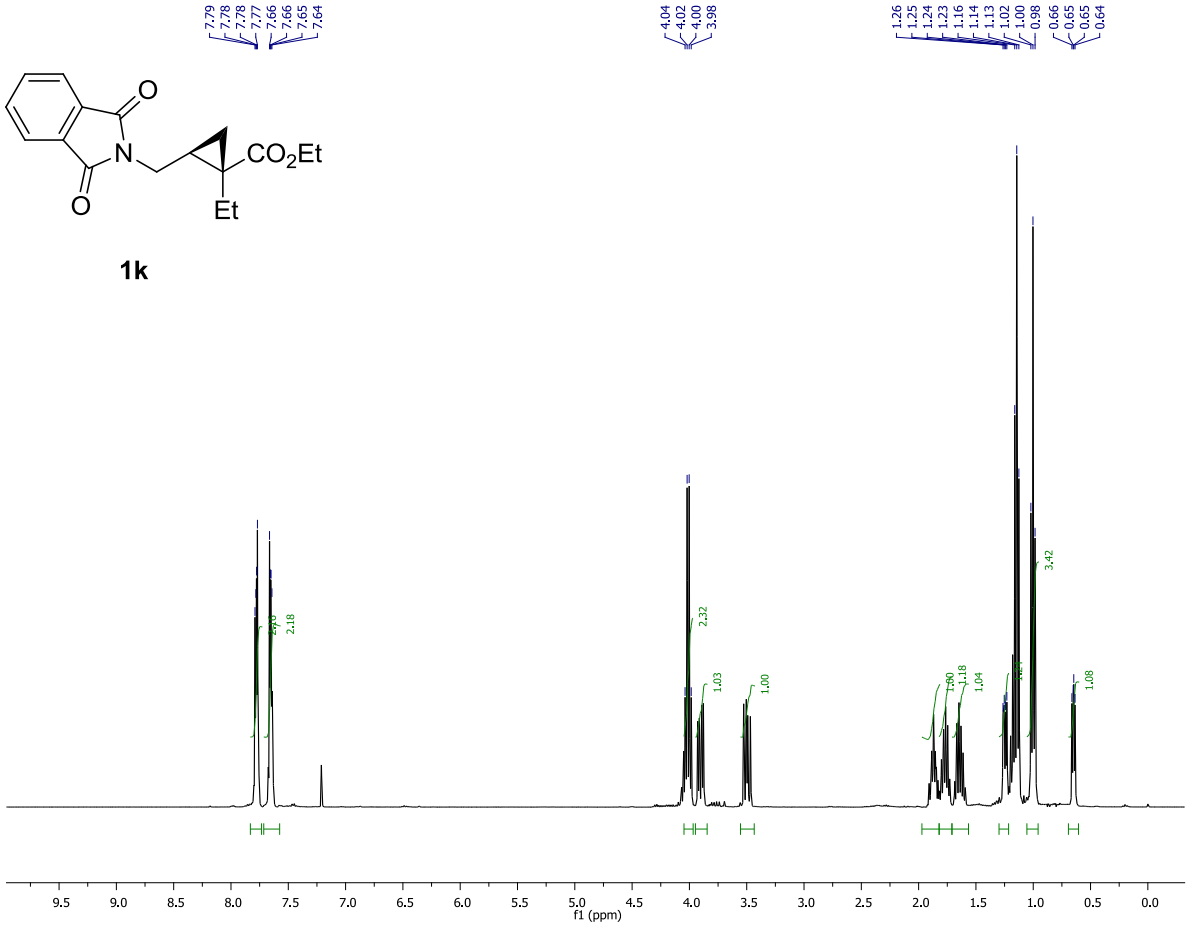

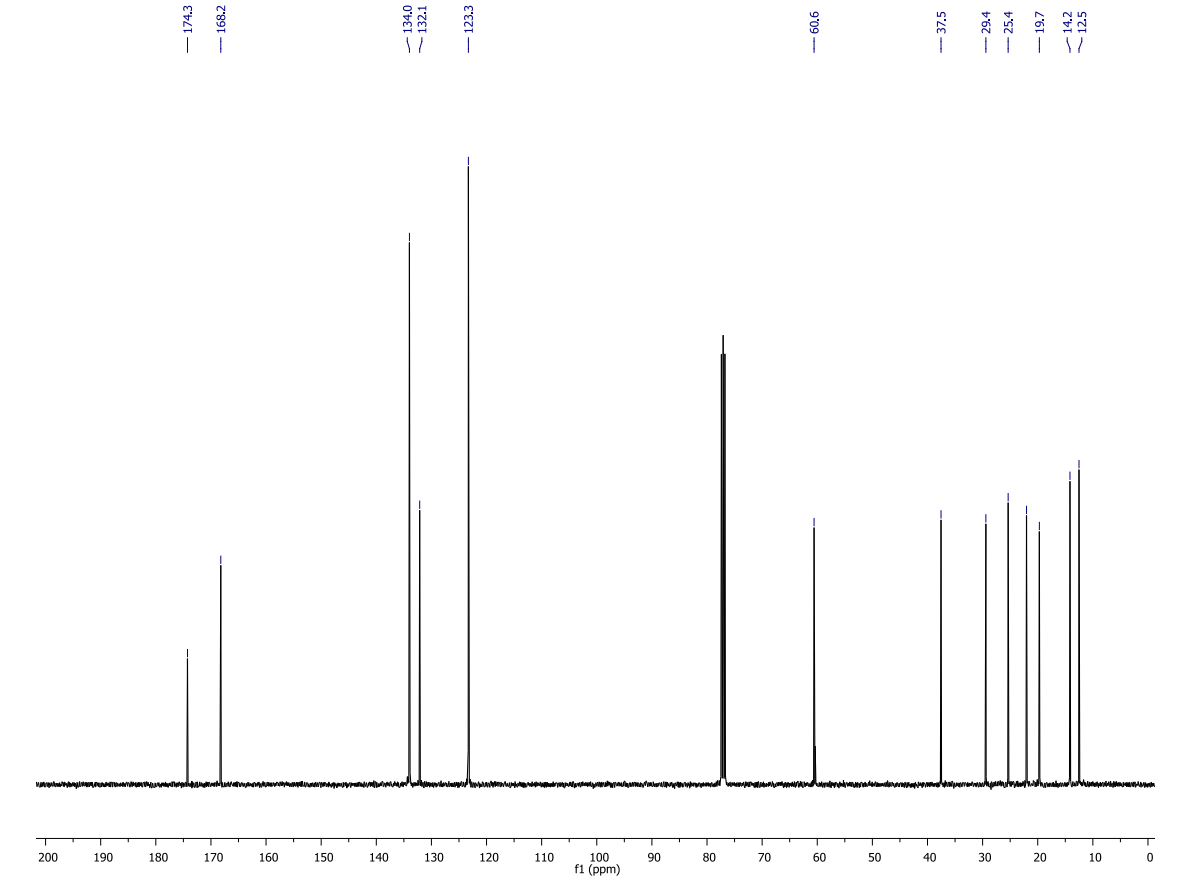

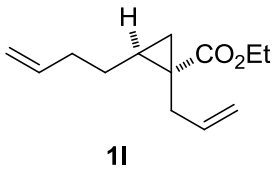

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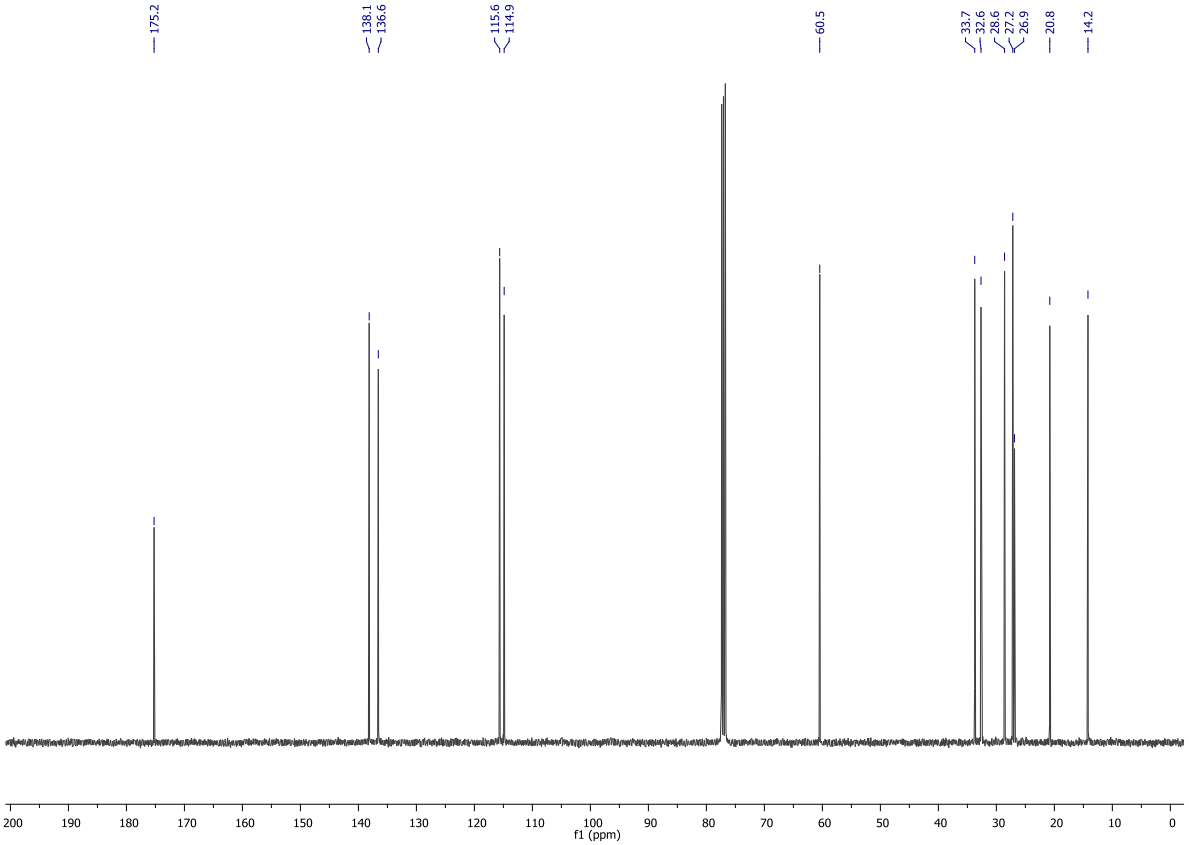

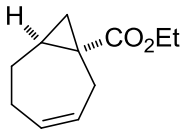

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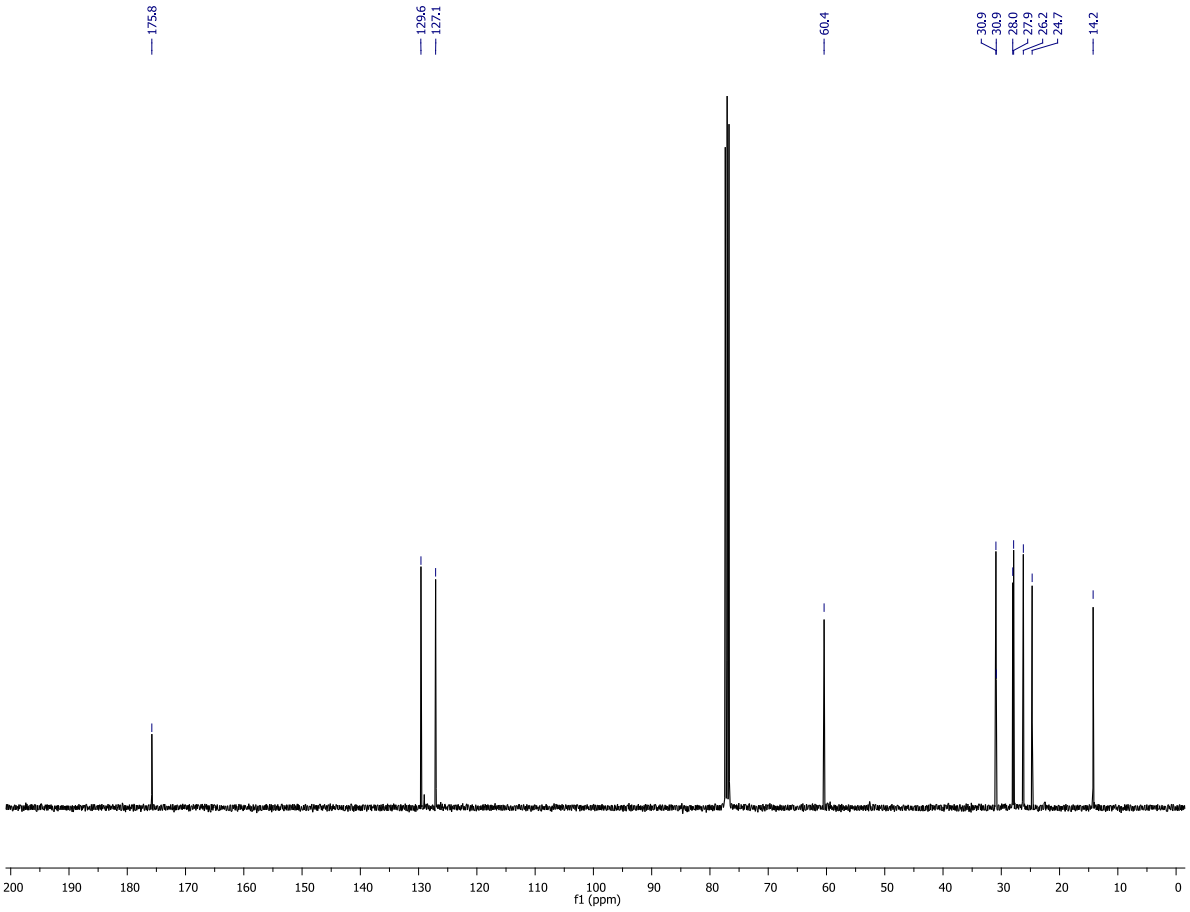
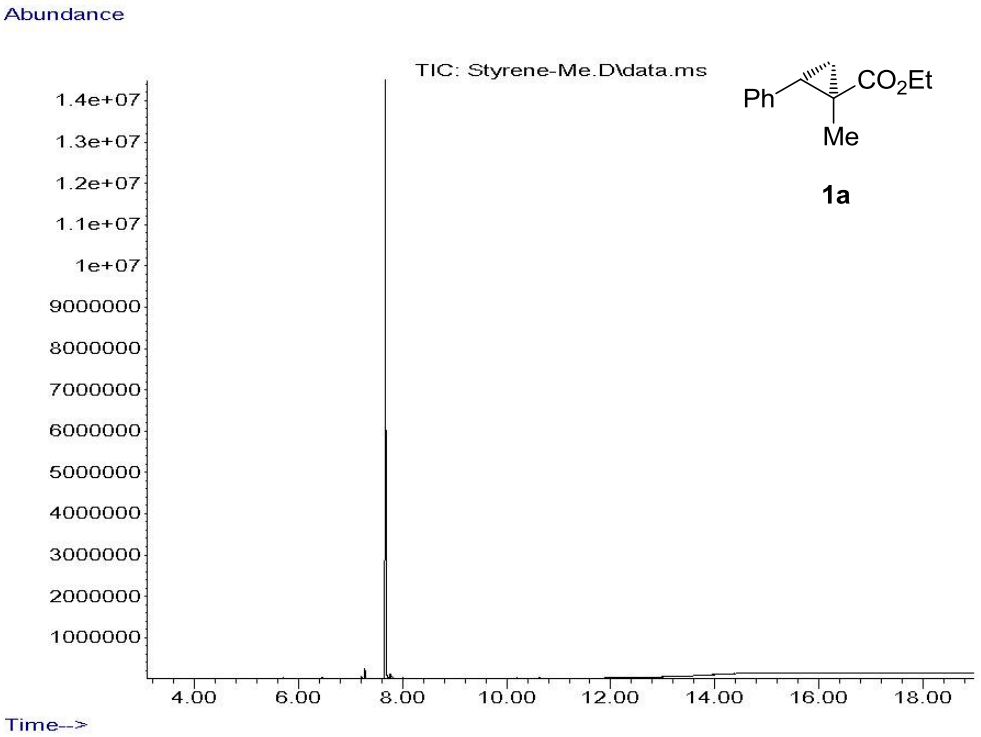


GC/MS Analysis of Compounds



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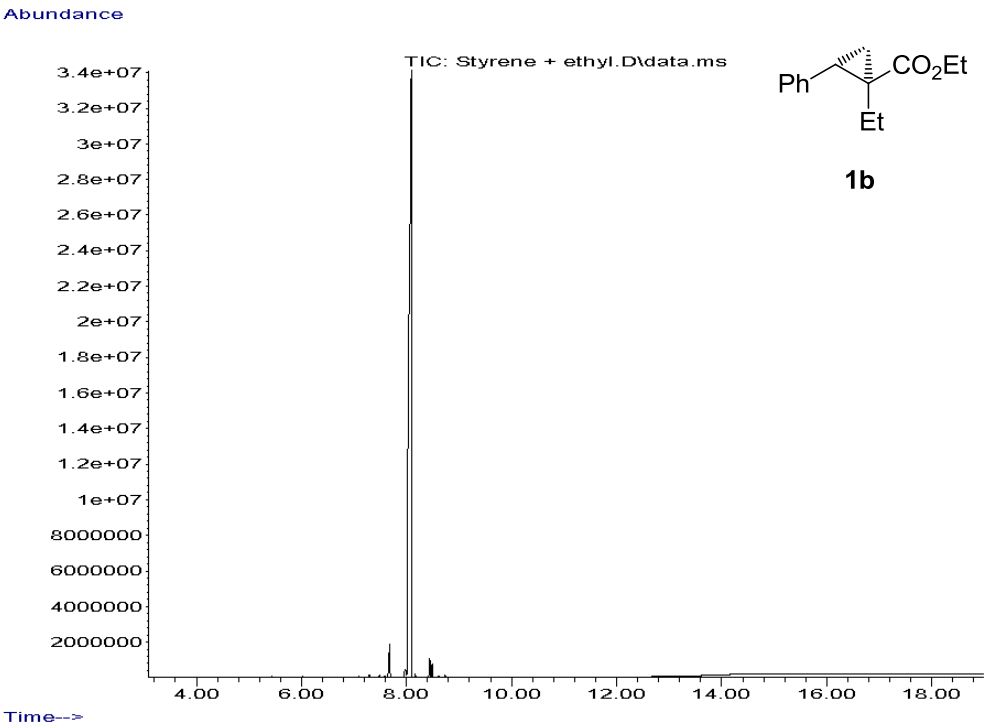

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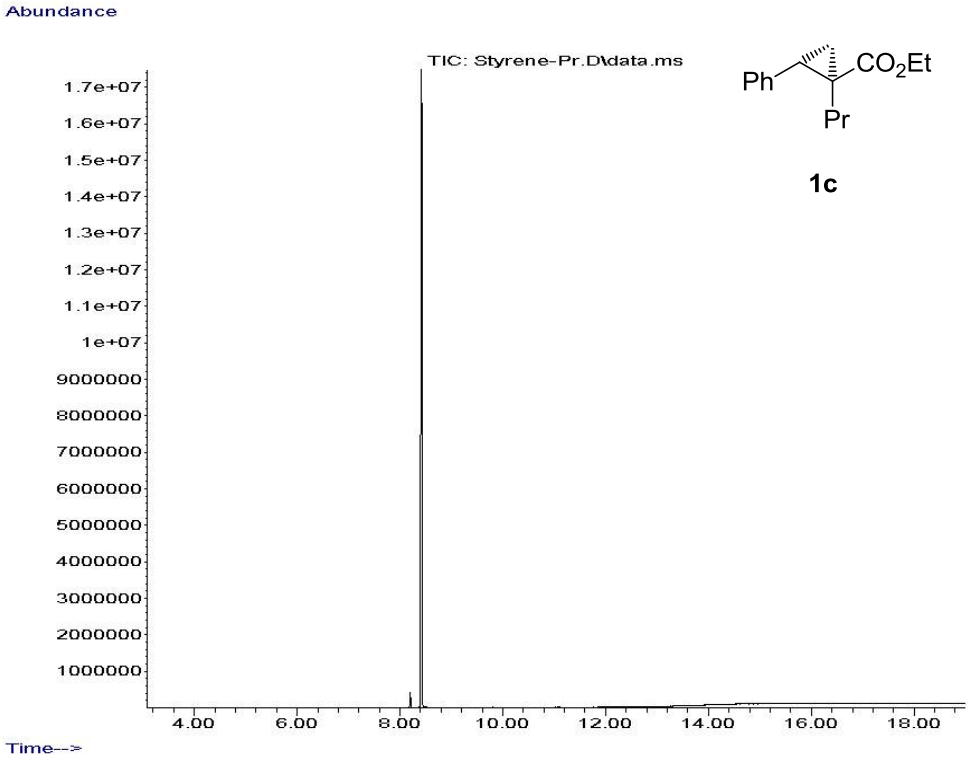

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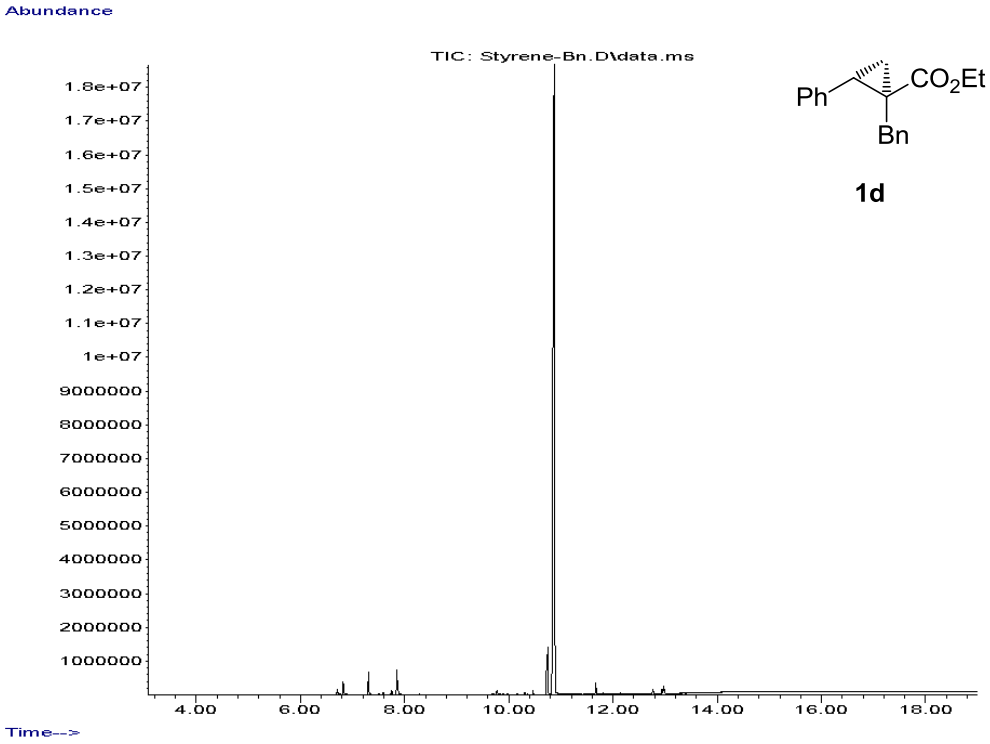

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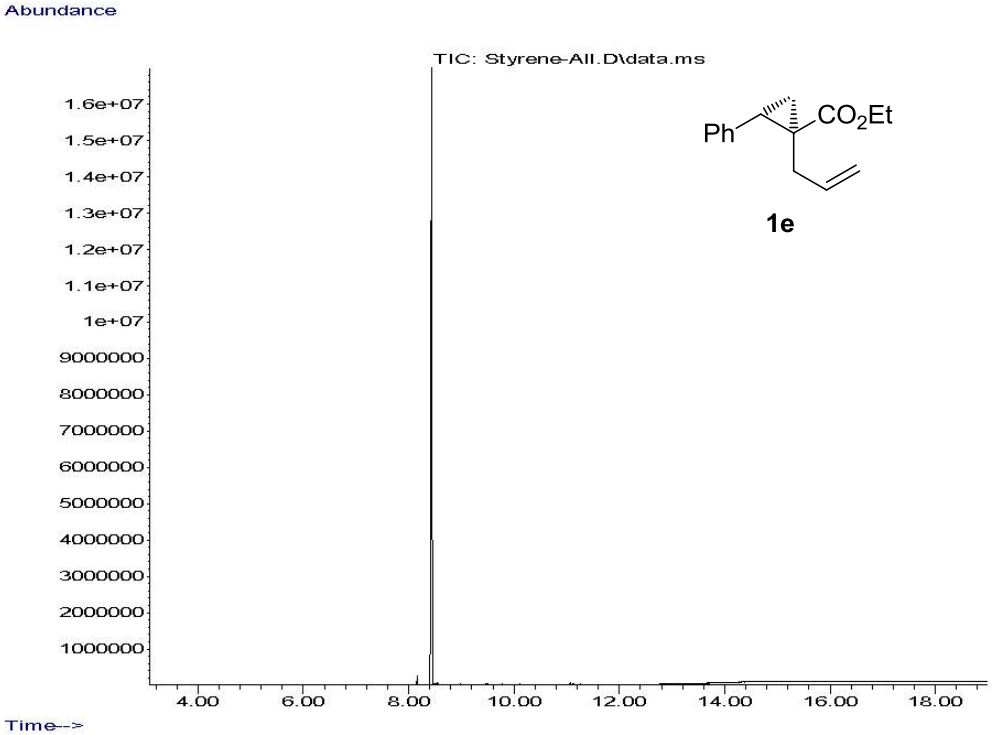

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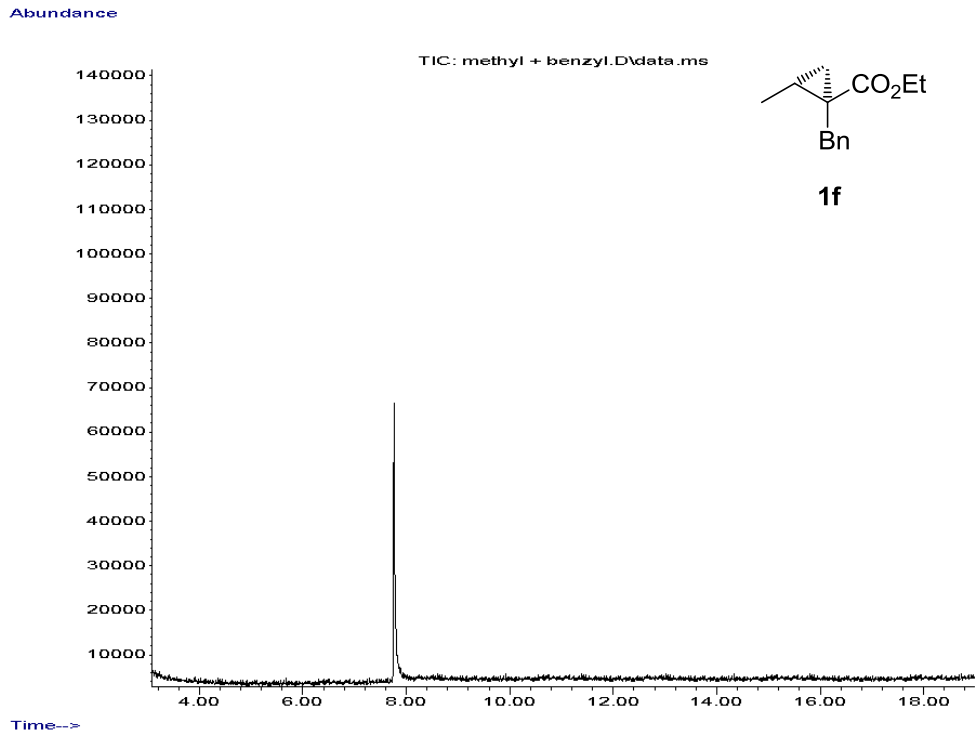

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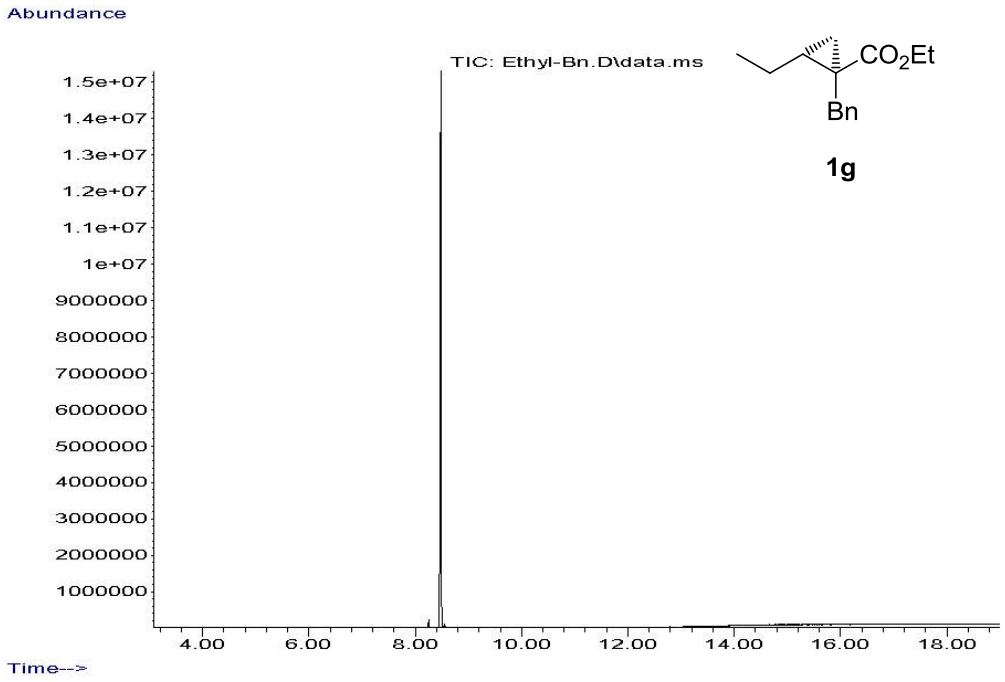

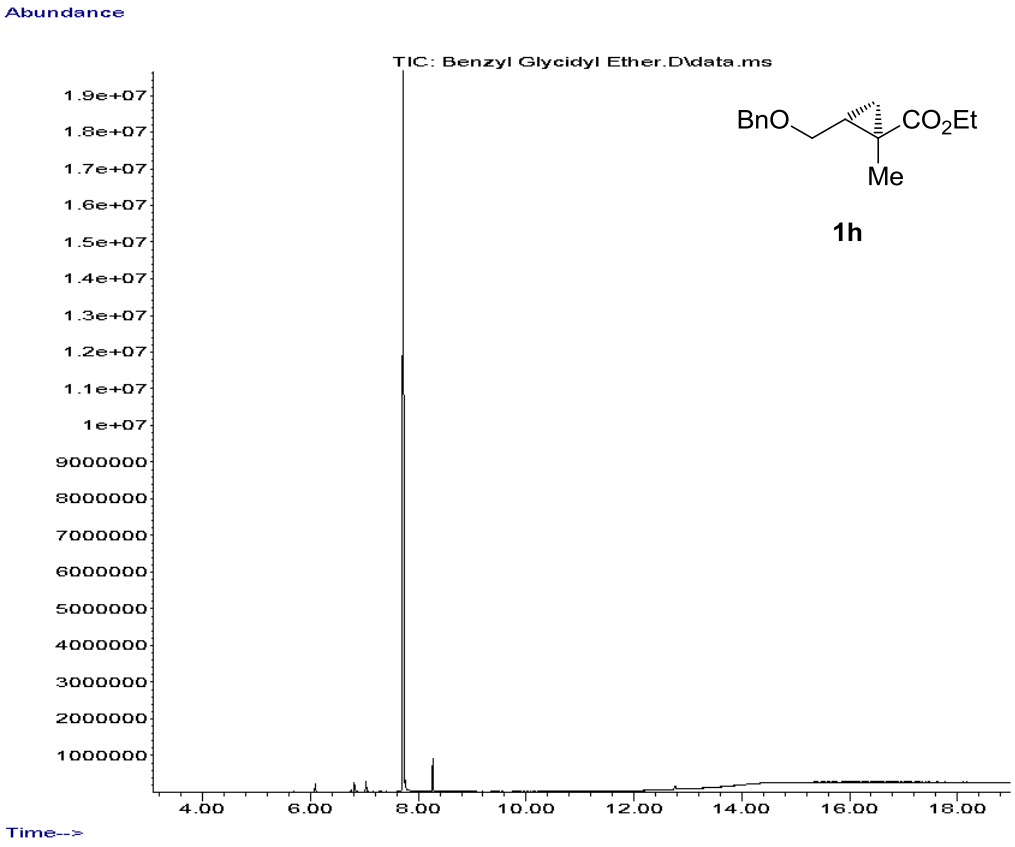

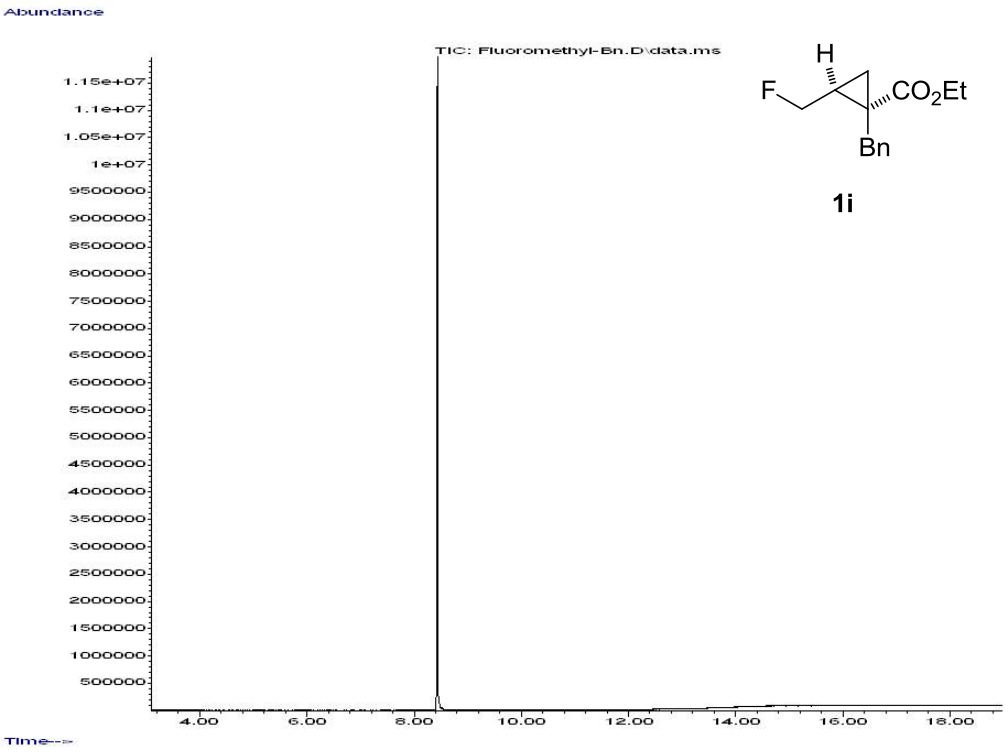

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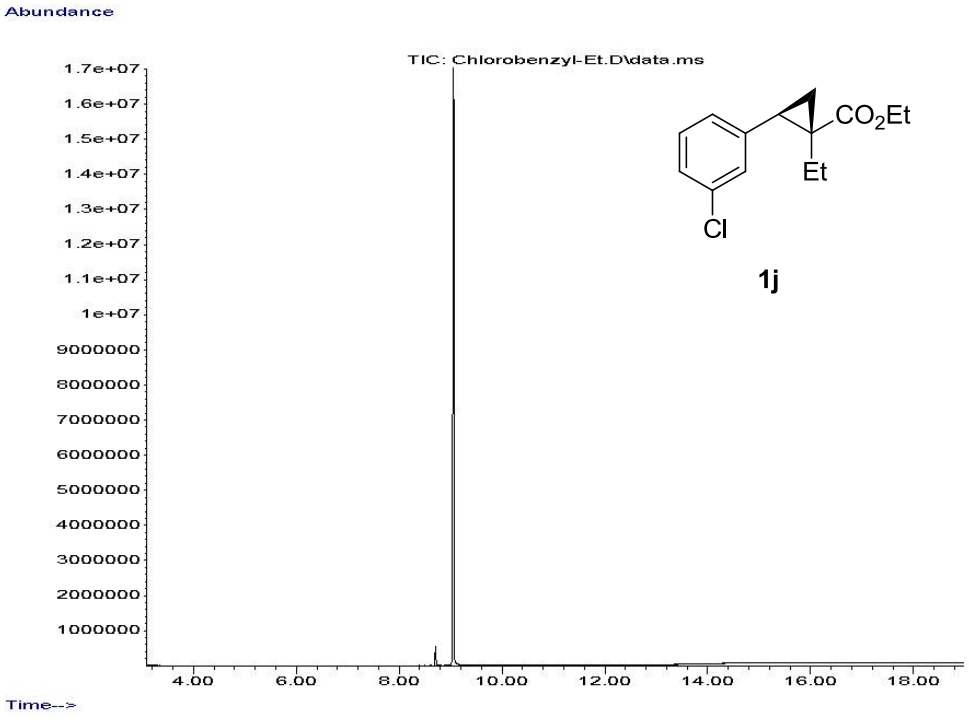
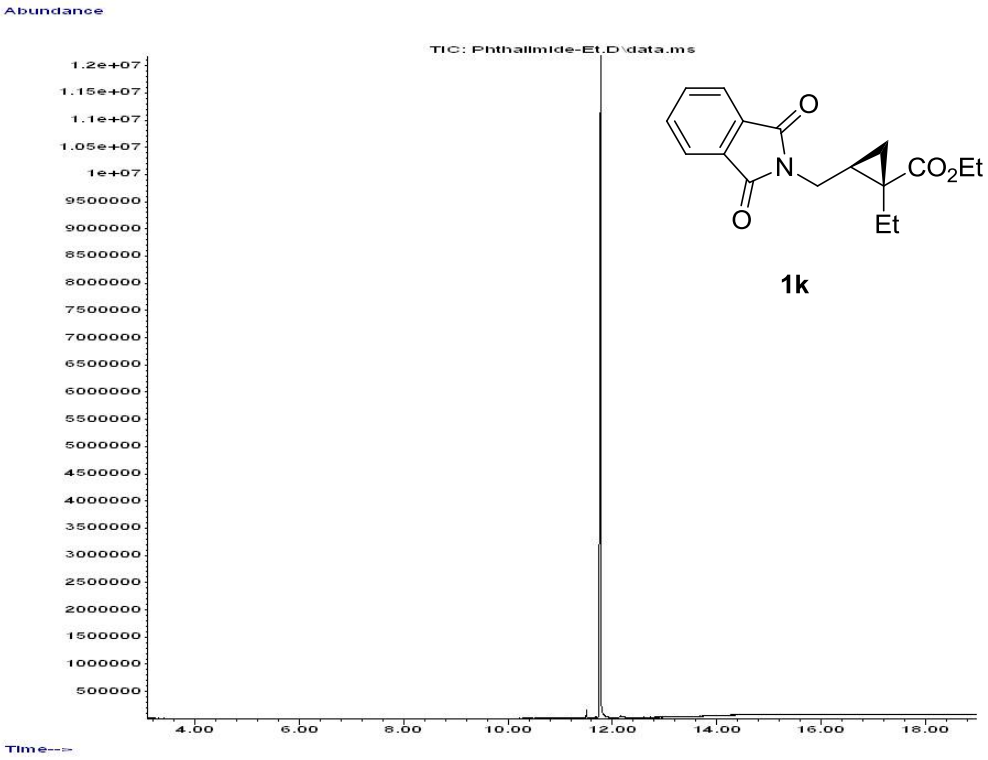


1j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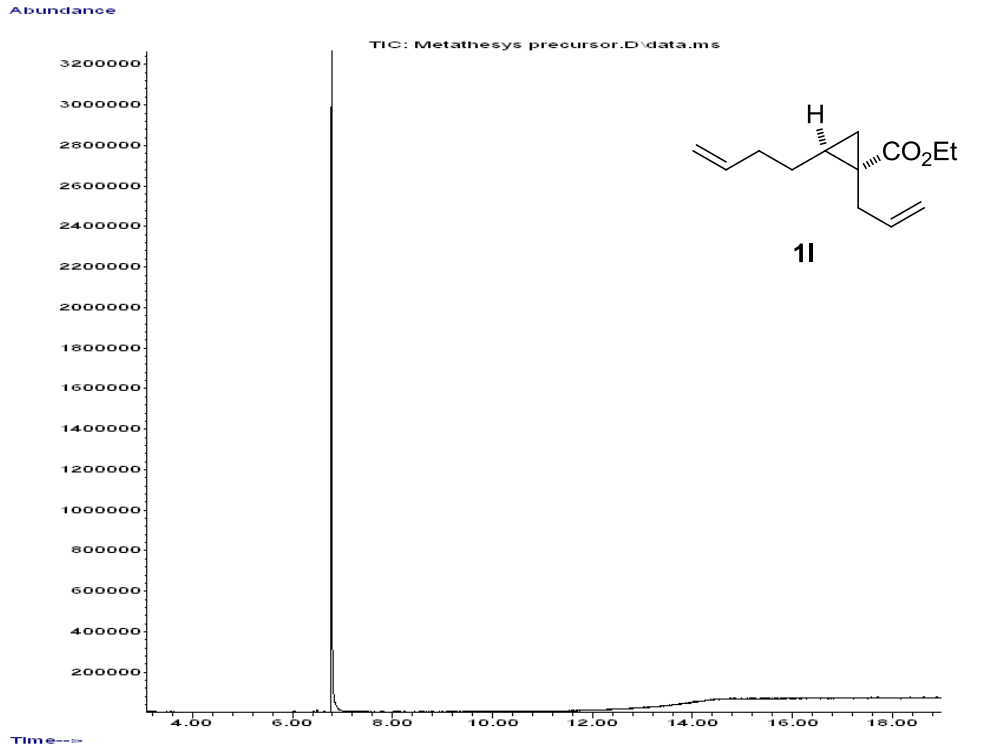
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