Stereoselective Formation of Alkenyl Halides via Magnesium Halide-Promoted Ring-Opening of Bis-Activated Cyclopropenes

Yi Wang and Hon Wai Lam*

School of Chemistry, University of Edinburgh, Joseph Black Building, The King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom

Supporting Information

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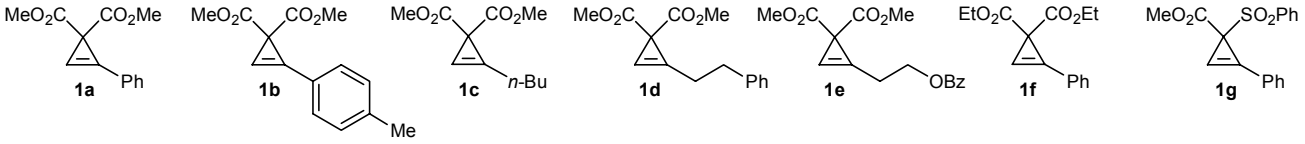
General Information

All non-aqueous reactions were carried out under a nitrogen atmosphere in oven-dried apparatus. THF and MeCN were dried and purified by passage through activated alumina columns using a solvent purification system from www.glasscontoursolventsystems.com. All other commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien $60F_{254}$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using potassium permanganate or ceric ammonium molybdate solution as appropriate. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron) employing the method of Still and co-workers.[1] Infra-red spectra were recorded as a thin film on sodium chloride plates or as a dilute solution in $CHCl_3$. ^1H NMR spectra were recorded on 500 MHz spectrometer or a 360 MHz spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal

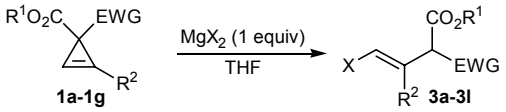
standard ($CDCl_3$ at 7.27 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a 250 MHz (62.9 MHz for ^{13}C) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°.

Preparation of Cyclopropenes

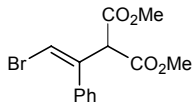


Cyclopropenes **1a**,[2] **1b**,[3] **1c**,[4] **1d**,[5] **1e**,[6] **1f**,[7] and **1g**[5] were prepared according to previously reported procedures.

Magnesium Halide-Promoted−Ring-Opening Reactions: General Procedure A



A solution of the appropriate cyclopropene (0.20 mmol) in THF (1 mL + 1 mL rinse) was added via cannula to a vial containing the appropriate magnesium halide (0.20 mmol) and a stirrer bar. The resulting mixture was stirred at the indicated temperature for the indicated time, and then filtered through a short plug of SiO_2 (*ca.* 4 cm high x 2 cm diameter) using EtOAc as eluent (*ca.* 50 mL). After the filtrate was concentrated *in vacuo*, purification of the residue by column chromatography afforded the alkenyl halide product.

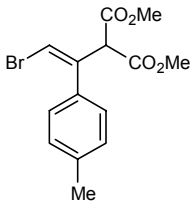


(*Z*)-Dimethyl 2-(2-bromo-1-phenylvinyl)malonate (3a). *On a 0.20 mmol scale:* The title compound was prepared according to General Procedure A from cyclopropene **1a** (46 mg, 0.20 mmol) and $MgBr_2$ (37 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (60 mg, 96%).

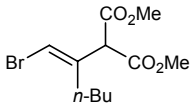
On a 2.00 mmol scale: A solution of the cyclopropene **1a** (2.00 mmol) in THF (15 mL + 5 mL rinse) was added via cannula over 2 min to a flask containing $MgBr_2$ (368 mg, 2.00 mmol) and a stirrer bar. The resulting mixture was stirred at room temperature for 30 min, and then filtered through a short plug of SiO_2 (*ca.* 4 cm high x 2 cm diameter) using EtOAc as eluent (*ca.* 100 mL). After the filtrate was

concentrated *in vacuo*, purification of the residue by column chromatography (hexane→5% EtOAc/hexane) afforded the *alkenyl bromide* **3a** (601 mg, 96%) as a colorless oil.

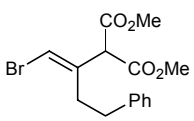
IR (film) 2954, 2846, 1738 (C=O), 1620, 1491, 1437, 1265, 1201, 1151, 1076 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.41-7.38 (2H, m, Ar**H**), 7.36-7.31 (3H, m, Ar**H**), 6.75 (1H, d, *J* = 0.6 Hz, =C**H**), 4.50 (1H, d, *J* =0.6 Hz, C**H**$(CO_2CH_3)_2$), 3.76 (6H, s, 2 x OC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.1 (2 x C), 138.1 (C), 137.2 (C), 128.4 (2 x CH), 128.3 (2 x CH), 128.2 (CH), 110.6 (CH), 58.8 (CH), 52.9 (2 x CH_3); HRMS (EI) Exact mass calcd for $C_{13}H_{13}{}^{79}BrO_4$ [M^+]: 311.9992, found: 311.9992.



(*Z*)-Dimethyl 2-(2-bromo-1-*p*-tolylvinyl)malonate (3b). The title compound was prepared according to General Procedure A from cyclopropene **1b** (49 mg, 0.20 mmol) and $MgBr_2$ (37 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (47 mg, 72%). IR (film) 2954, 1739 (C=O), 1616, 1510, 1435, 1308, 1196, 1151, 1022, 976 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.20 (4H, s, Ar**H**), 6.71 (1H, s, =C**H**), 4.48 (1H, s, C**H**$(CO_2CH_3)_2$), 3.76 (6H, s, 2 x OC**H**$_3$), 2.37 (3H, s, ArC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.2 (2 x C), 138.1 (C), 137.2 (C), 135.1 (C), 129.0 (2 x CH), 128.2 (2 x CH), 110.2 (CH), 58.9 (CH), 52.9 (2 x CH_3), 21.2 (CH_3); HRMS (EI) Exact mass calcd for $C_{14}H_{15}{}^{79}BrO_4$ [M^+]: 326.0148, found: 326.0151.

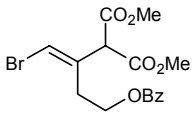


(*E*)-Dimethyl 2-[1-(1-bromomethylidene)pentyl]malonate (3c). The title compound was prepared according to General Procedure A from cyclopropene **1c** (42 mg, 0.20 mmol) and $MgBr_2$ (37 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (44 mg, 75%). IR (film) 2956, 2871, 1739 (C=O), 1626, 1456, 1435, 1379, 1308, 1273, 1198 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.36 (1H, d, *J* = 0.5 Hz, =C**H**), 4.16 (1H, d, *J* = 0.5 Hz, C**H**$(CO_2CH_3)_2$), 3.75 (6H, s, 2 x OC**H**$_3$), 2.36-2.32 (2H, m, =CC**H**$_2$), 1.44-1.28 (4H, m, C**H**$_2$C**H**$_2$CH$_3$), 0.91 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.4 (2 x C), 137.2 (C), 109.2 (CH), 56.9 (CH), 52.8 (2 x CH_3), 33.1 (CH_2), 28.9 (CH_2), 22.5 (CH_2), 13.8 (CH_3); HRMS (EI) Exact mass calcd for $C_{11}H_{17}{}^{79}BrO_4$ [M^+]: 292.0305, found: 292.0304.

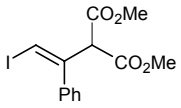


(*E*)-Dimethyl 2-[1-(1-bromomethylidene)-3-phenylpropyl]malonate (3d). The title compound was prepared according to General Procedure A from cyclopropene **1d** (52 mg, 0.20 mmol) and $MgBr_2$ (37 mg, 0.20 mmol) at room temperature for 2 h and

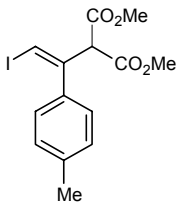
purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (59 mg, 87%). IR (film) 3028, 2954, 1738 (C=O), 1624, 1495, 1437, 1269, 1201, 1153, 1026 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.33-7.29 (2H, m, Ar**H**), 7.26-7.20 (3H, m, Ar**H**), 6.46 (1H, br s, =C**H**), 4.18 (1H, d, *J* = 0.5 Hz, C**H**$(CO_2CH_3)_2$), 3.78 (6H, s, 2 x OC**H**$_3$), 2.79-2.73 (2H, m, C**H**$_2$Ph), 2.69-2.63 (2H, m, C**H**$_2$$CH_2$Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.3 (2 x C), 141.0 (C), 136.4 (C), 128.4 (2 x CH), 128.3 (2 x CH), 126.1 (CH), 110.3 (CH), 57.4 (CH), 52.9 (2 x CH_3), 35.3 (CH_2), 33.0 (CH_2); HRMS (EI) Exact mass calcd for $C_{15}H_{17}{}^{79}BrO_4$ [M^+]: 340.0305, found: 340.0302.



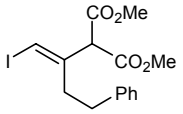
(*E*)-Dimethyl 2-[3-benzoyloxy-1-(1-bromomethylidene)propyl]malonate (3e). The title compound was prepared according to General Procedure A from cyclopropene **1e** (61 mg, 0.20 mmol) and $MgBr_2$ (37 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (64 mg, 84%). IR (film) 2956, 2362, 1720 (C=O), 1602, 1437, 1383, 1273, 1201, 1153, 1113 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 8.06-8.03 (2H, m, Ar**H**), 7.58-7.54 (1H, m, Ar**H**), 7.46-7.42 (2H, m, Ar**H**), 6.58 (1H, s, =C**H**), 4.45 (2H, t, *J* = 7.0 Hz, C**H**$_2$O), 4.31 (1H, s, C**H**$(CO_2CH_3)_2$), 3.73 (6H, s, 2 x OC**H**$_3$), 2.88 (2H, t, *J* = 7.0 Hz, =CC**H**$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.1 (2 x C), 166.3 (C), 133.1 (C), 132.9 (CH), 130.0 (C), 129.6 (2 x CH), 128.3 (2 x CH), 112.2 (CH), 61.7 (CH_2), 57.2 (CH), 53.0 (2 x CH_3), 32.6 (CH_2); HRMS (ES) Exact mass calcd for $C_{16}H_{18}{}^{79}BrO_6$ [$M+H^+$]: 385.0281, found: 385.0285.



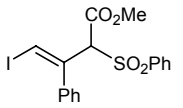
(*Z*)-Dimethyl 2-(2-iodo-1-phenylvinyl)malonate (3f). The title compound was prepared according to General Procedure A from cyclopropene **1a** (46 mg, 0.20 mmol) and MgI_2 (56 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a 9:1 mixture of inseparable geometric isomers as a colorless oil (70 mg, 97%). IR (film) 3058, 2952, 2846, 1739 (C=O), 1597, 1491, 1437, 1307, 1265, 1153 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.39-7.32 (3H, m, Ar**H**), 7.25-7.22 (2H, m, Ar**H**), 6.87 (1H, d, *J* = 0.6 Hz, =C**H**), 4.51 (1H, d, *J* = 0.6 Hz, C**H**$(CO_2CH_3)_2$), 3.72 (6H, s, 2 x OC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.0 (2 x C), 142.8 (C), 141.0 (C), 128.4 (2 x CH), 128.2 (3 x CH), 84.8 (CH), 59.4 (CH), 52.9 (2 x CH_3); HRMS (EI) Exact mass calcd for $C_{13}H_{13}IO_4$ [M^+]: 359.9853, found: 359.9852.



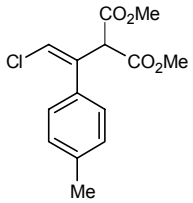
(*Z*)-Dimethyl 2-(2-bromo-1-*p*-tolylvinyl)malonate (3g). The title compound was prepared according to General Procedure A from cyclopropene **1b** (49 mg, 0.20 mmol) and MgI_2 (56 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (70 mg, 94%). IR (film) 2952, 1738 (C=O), 1612, 1508, 1435, 1309, 1198, 1151, 1022, 974 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.20 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.16 (2H, dm, *J* = 8.1 Hz, Ar**H**), 6.87 (1H, br s, =C**H**), 4.53 (1H, s, C**H**$(CO_2CH_3)_2$), 3.75 (6H, s, 2 x OC**H**$_3$), 2.37 (3H, s, ArC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.1 (2 x C), 142.8 (C), 138.1 (C), 138.0 (C), 129.1 (2 x CH), 128.1 (2 x CH), 84.4 (CH), 59.5 (CH), 52.9 (2 x CH_3), 21.3 (CH_3); HRMS (ES) Exact mass calcd for $C_{14}H_{16}IO_4$ $[M+H]^+$: 375.0088, found: 375.0092.



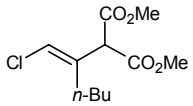
(*E*)-Dimethyl 2-[1-(1-iodomethylidene)-3-phenylpropyl]malonate (3h). The title compound was prepared according to General Procedure A from cyclopropene **1d** (52 mg, 0.20 mmol) and MgI_2 (56 mg, 0.20 mmol) at room temperature for 2 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (77 mg, 99%). IR (film) 2956, 2254, 1736 (C=O), 1437, 1265, 1153, 1028, 908, 733, 650 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.19 (5H, m, Ar**H**), 6.57 (1H, s, =C**H**), 4.26 (1H, s, C**H**$(CO_2CH_3)_2$), 3.75 (6H, s, 2 x OC**H**$_3$), 2.74-2.71 (2H, m, C**H**$_2$Ph), 2.65-2.62 (2H, C**H**$_2$CH$_2$Ph); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.2 (2 x C), 141.1 (C), 140.8 (C), 128.4 (2 x CH), 128.3 (2 x CH), 126.2 (CH), 84.2 (CH), 57.8 (CH), 52.9 (2 x CH_3), 39.6 (CH_2), 33.0 (CH_2); HRMS (ES) Exact mass calcd for $C_{15}H_{21}NIO_4$ $[M+NH_4]^+$: 406.0510, found: 406.0507.



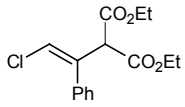
(*E*)-Methyl 4-iodo-3-phenyl-2-(phenylsulfonyl)but-3-enoate (3i). The title compound was prepared according to General Procedure A from cyclopropene **1g** (63 mg, 0.20 mmol) and MgI_2 (56 mg, 0.20 mmol) at room temperature for 2 h and then at 40 °C for 6 h. Purification of the residue by column chromatography (5%→10% EtOAc/hexane) gave a yellow oil (68 mg, 77%). IR (film) 3062, 2952, 1745 (C=O), 1585, 1491, 1446, 1329, 1147, 1082, 910 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.91-7.88 (2H, m, Ar**H**), 7.72-7.67 (1H, m, Ar**H**), 7.58-7.54 (2H, m, Ar**H**), 7.35 (1H, s, =C**H**), 7.34-7.32 (3H, m, Ar**H**), 7.13-7.11 (2H, m, Ar**H**), 5.05 (1H, s, C**H**CO_2CH_3), 3.73 (3H, s, OC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 164.4 (C), 141.2 (C), 141.5 (C), 137.6 (C), 134.5 (CH), 129.9 (2 x CH), 129.0 (2 x CH), 128.5 (3 x CH), 128.0 (2 x CH), 90.1 (CH), 74.4 (CH), 53.4 (CH_3); HRMS (ES) Exact mass calcd for $C_{17}H_{19}INO_4S$ $[M+NH_4]^+$: 460.0074, found: 460.0067.



(*Z*)-Dimethyl 2-(2-chloro-1-*p*-tolylvinyl)malonate (3j). The title compound was prepared according to General Procedure A from cyclopropene **1b** (49 mg, 0.20 mmol) and $MgCl_2$ (19 mg, 0.20 mmol) at 40 °C for 18 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a ~16:1 inseparable mixture of regioisomers as a colorless oil (43 mg, 76%). IR ($CHCl_3$) 3028, 2954, 1739 (C=O), 1611, 1511, 1435, 1310, 1197, 1152, 1024 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.24-7.18 (4H, m, Ar**H**), 6.53 (1H, s, =C**H**), 4.46 (1H, s, C**H**$(CO_2CH_3)_2$), 3.76 (6H, s, 2 x OC**H**$_3$), 2.37 (3H, s, ArC**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.4 (2 x C), 138.1 (C), 134.3 (C), 133.6 (C), 129.0 (2 x CH), 128.4 (2 x CH), 120.8 (CH), 58.0 (CH), 52.9 (2 x CH_3), 21.2 (CH_3); HRMS (ES) Exact mass calcd for $C_{14}H_{16}{}^{35}ClO_4$ $[M+H]^+$: 283.0732, found: 283.0728.

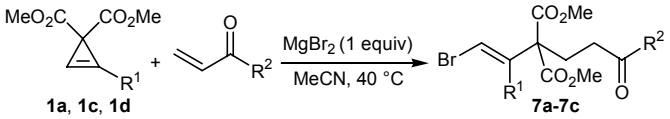


(*E*)-Dimethyl 2-[1-(1-chloromethylidene)pentyl]malonate (3k). The title compound was prepared according to General Procedure A from cyclopropene **1c** (42 mg, 0.20 mmol) and $MgCl_2$ (19 mg, 0.20 mmol) at 40 °C for 18 h and purified by column chromatography (5% EtOAc/hexane) to give a ~16:1 inseparable mixture of regioisomers as a colorless oil (43 mg, 85%). IR ($CHCl_3$) 2957, 2873, 1740 (C=O), 1634, 1436, 1308, 1199, 1150, 1027, 948 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.20 (1H, s, =C**H**), 4.11 (1H, s, C**H**$(CO_2CH_3)_2$), 3.75 (6H, s, 2 x OC**H**$_3$), 2.35-2.31 (2H, m, =CC**H**$_2$), 1.42-1.32 (4H, m, C**H**$_2$C**H**$_2$$CH_3$), 0.91 (3H, t, J = 7.1 Hz, CH_2C**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.7 (2 x C), 134.7 (C), 119.8 (CH), 56.1 (CH), 52.8 (2 x CH_3), 30.6 (CH_2), 28.9 (CH_2), 22.5 (CH_2), 13.8 (CH_3); HRMS (ES) Exact mass calcd for $C_{11}H_{18}{}^{35}ClO_4$ $[M+H]^+$: 249.0888, found: 249.0886.

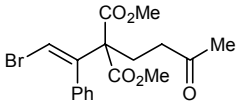


(*Z*)-Diethyl 2-(2-chloro-1-phenylvinyl)malonate (3l). The title compound was prepared according to General Procedure A from cyclopropene **1f** (52 mg, 0.20 mmol) and $MgCl_2$ (19 mg, 0.20 mmol) at 40 °C for 18 h and purified by column chromatography (hexane→5% EtOAc/hexane) to give a colorless oil (37 mg, 62%). IR (film) 2983, 1734 (C=O), 1493, 1444, 1367, 1306, 1151, 1095, 1032, 920 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.41-7.31 (5H, m, Ar**H**), 6.56 (1H, d, J = 0.6 Hz, =C**H**), 4.44 (1H, d, J = 0.6 Hz, C**H**$(CO_2CH_2CH_3)_2$), 4.26-4.16 (4H, m, 2 x OC**H**$_2$), 1.25 (6H, t, J = 7.2 Hz, 2 x OCH_2C**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 167.0 (2 x C), 136.7 (C), 134.7 (C), 128.6 (2 x CH), 128.3 (2 x CH), 128.1 (CH), 120.9 (CH), 62.0 (2 x CH_2), 58.3 (CH), 13.9 (2 x CH_3); HRMS (ES) Exact mass calcd for $C_{15}H_{21}ClO_4N$ $[M+NH_4]^+$: 314.1154, found: 314.1157.

One-Pot Magnesium Halide-Promoted Ring-Opening–Michael Reactions: General Procedure B



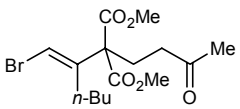
A solution of the appropriate cyclopropene (0.20 mmol) in MeCN (1 mL + 1 mL rinse) was added *via* cannula to a vial containing the appropiate enone (0.40 mmol), $MgBr_2$ (37 mg, 0.20 mmol), and a stirrer bar. The resulting mixture was stirred at 40 °C for 18 h. After cooling to room temperature, the mixture was filtered through a short plug of SiO_2 (*ca.* 4 cm high x 2 cm diameter) using EtOAc as eluent (*ca.* 50 mL) and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography afforded the alkenyl halide product.



(*Z*)-Dimethyl 2-(2-bromo-1-phenylvinyl)-2-(3-oxobutyl)malonate (7a). *On a 0.20 mmol scale:* The title compound was prepared according to General Procedure B from cyclopropene **1a** (46 mg, 0.20 mmol) and methyl vinyl ketone (32 μL, 0.40 mmol) and purified by column chromatography (10%→30% EtOAc/hexane) to give a 19:1 inseparable mixture of regioisomers as a colorless oil (60 mg, 78%).

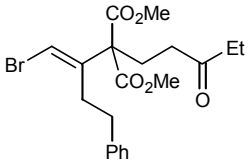
On an 8.00 mmol scale: A solution of the cyclopropene **1a** (1.86 g, 8.00 mmol) in MeCN (40 mL + 10 mL rinse) was added via cannula over 5 min to a flask containing methyl vinyl ketone (1.22 mL, 15.0 mmol). The resulting mixture was stirred at room temperature for 30 min and then at 40 °C for 17.5 h. After cooling to room temperature, the mixture was filtered through a short pad of SiO_2 (*ca.* 4 cm high x 6 cm diameter) using EtOAc as eluent (*ca.* 100 mL) and the filtrate was concentrated *in vacuo*. Purification of the residue by column chromatography (10%→30% EtOAc/hexane) gave the *alkenyl bromide* **7a** as a 19:1 inseparable mixture of regioisomers (2.34 g, 76%) as a colorless oil.

IR ($CHCl_3$) 2953, 1735 (C=O), 1613, 1491, 1437, 1366, 1254, 1171, 1092, 1030 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.38-7.31 (3H, m, Ar**H**), 7.07-7.05 (2H, m, Ar**H**), 6.92 (1H, s, =C**H**), 3.71 (6H, s, 2 x OC**H**$_3$), 2.53-2.50 (2H, m, C**H**$_2$C**H**$_2$C=O), 2.27-2.24 (2H, m, C**H**$_2$C**H**$_2$C=O), 2.09 (3H, s, C**H**$_3$C=O); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 206.6 (C), 169.5 (2 x C), 141.4 (C), 137.1 (C), 128.8 (2 x CH), 128.3 (2 x CH), 128.2 (CH), 112.3 (CH), 63.7 (C), 52.8 (2 x CH_3), 39.0 (CH_2), 29.9 (CH_3), 28.2 (CH_2); HRMS (ES) Exact mass calcd for $C_{17}H_{20}{}^{79}BrO_5$ $[M+H]^+$: 383.0489, found: 383.0492.



(*E*)-Dimethyl 2-[1-(1-bromomethylidine)pentyl]-2-(3-oxobutyl)malonate (7b). The title compound was prepared according to General Procedure B from cyclopropene **1c** (43 mg, 0.20 mmol) and methyl vinyl ketone (32 μL, 0.40 mmol) and purified by

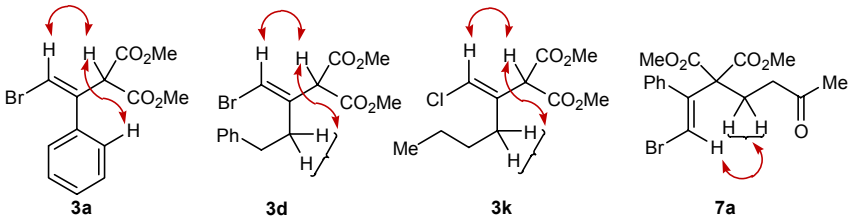
column chromatography (5%→10% EtOAc/hexane) to give a colorless oil (56 mg, 78%). IR ($CHCl_3$) 3105, 2956, 2872, 1734 (C=O), 1610, 1434, 1369, 1255, 1169, 1091 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 6.46 (1H, s, =C**H**), 3.73 (6H, s, 2 x OC**H**$_3$), 2.52-2.49 (2H, m, C**H**$_2$C=O), 2.34-2.31 (2H, m, =CC**H**$_2$), 2.18-2.14 (2H, m, C**H**$_2$CH$_2$C=O), 2.11 (3H, s, C**H**$_3$C=O), 1.44-1.38 (2H, m, C**H**$_2$CH$_2$CH$_3$), 1.36-1.28 (2H, m, C**H**$_2$CH$_3$), 0.90 (3H, t, *J* = 7.3 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 206.8 (C), 169.8 (2 x C), 140.5 (C), 109.5 (CH), 63.6 (C), 52.7 (2 x CH_3), 39.0 (CH_2), 32.5 (CH_2), 30.0 (CH_3), 29.6 (CH_2), 27.3 (CH_2), 23.1 (CH_2), 13.7 (CH_3); HRMS (ES) Exact mass calcd for $C_{15}H_{24}{}^{79}BrO_5$ $[M+H]^+$: 363.0802, found: 363.0799.



(*E*)-Dimethyl 2-[1-(1-bromomethylidine)-3-phenylpropyl]-2-(3-oxopentyl)malonate (7c). The title compound was prepared according to General Procedure B from cyclopropene **1d** (52 mg, 0.20 mmol) and ethyl vinyl ketone (40 μL, 0.40 mmol) and purified by column chromatography (5%→10% EtOAc/hexane) to give a colorless oil (61 mg, 72%). IR ($CHCl_3$) 2952, 1734 (C=O), 1496, 1455, 1242, 1095, 1031, 753, 700, 557 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 7.33-7.18 (5H, m, Ar**H**), 6.59 (1H, s, =C**H**), 3.76 (6H, s, 2 x OC**H**$_3$), 2.81-2.76 (2H, m, C**H**$_2$), 2.54-2.39 (8H, m, 4 x C**H**$_2$), 1.06 (3H, t, *J* = 7.3 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 209.4 (C), 169.6 (2 x C), 141.5 (C), 139.7 (C), 128.4 (2 x CH), 128.1 (2 x CH), 126.1 (CH), 110.4 (CH), 63.7 (C), 52.8 (2 x CH_3), 37.6 (CH_2), 36.0 (CH_2), 35.5 (CH_2), 33.4 (CH_2), 27.4 (CH_2), 7.7 (CH_3); HRMS (EI) Exact mass calcd for $C_{20}H_{26}{}^{79}BrO_5$ $[M+H]^+$: 425.0958, found: 425.0957.

Stereochemical Determinations

- The stereoselectivities of magnesium halide-Promoted ring-opening reactions producing alkenyl halides **3a**, **3d**, **3k**, and **7a** were assigned on the basis of NOESY experiments, which displayed the following diagnostic enhancements:

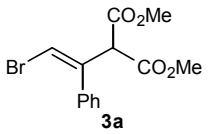


- The stereoselectivities of the remaining products were assigned by analogy.

References

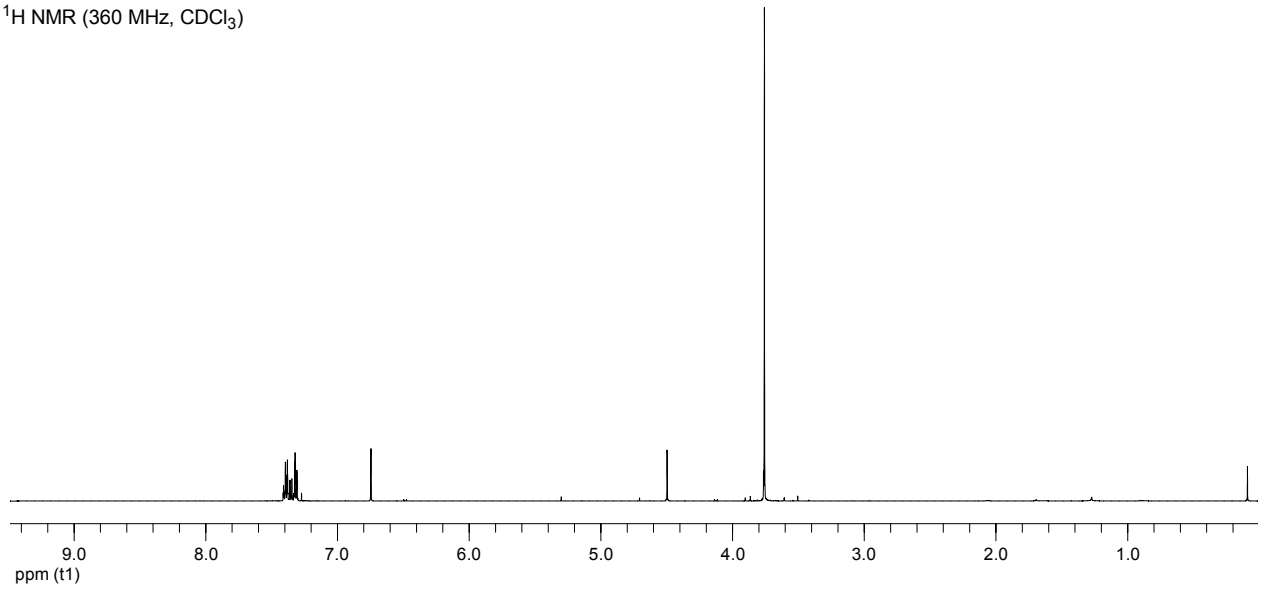
1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.
2. Liao, L.-a.; Zhang, F.; Yan, N.; Golen, J. A.; Fox, J. M. *Tetrahedron* **2004**, *60*, 1803–1816.
3. Chuprakov, S.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 3714–3715.
4. Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2003**, *125*, 7198–7199.
5. Wang, Y.; Fordyce, E. A. F.; Chen, F. Y.; Lam, H. W. *Angew. Chem.*, *Int. Ed.* **2008**, *47*, 7350–7353.
6. Fordyce, E. A. F.; Wang, Y.; Luebbers, T.; Lam, H. W. *Chem. Commun.* **2008**, 1124−1126.
7. Davies, H. M. L.; Romines, K. R. *Tetrahedron* **1998**, *44*, 3343–3348.

NMR Spectra of New Compounds

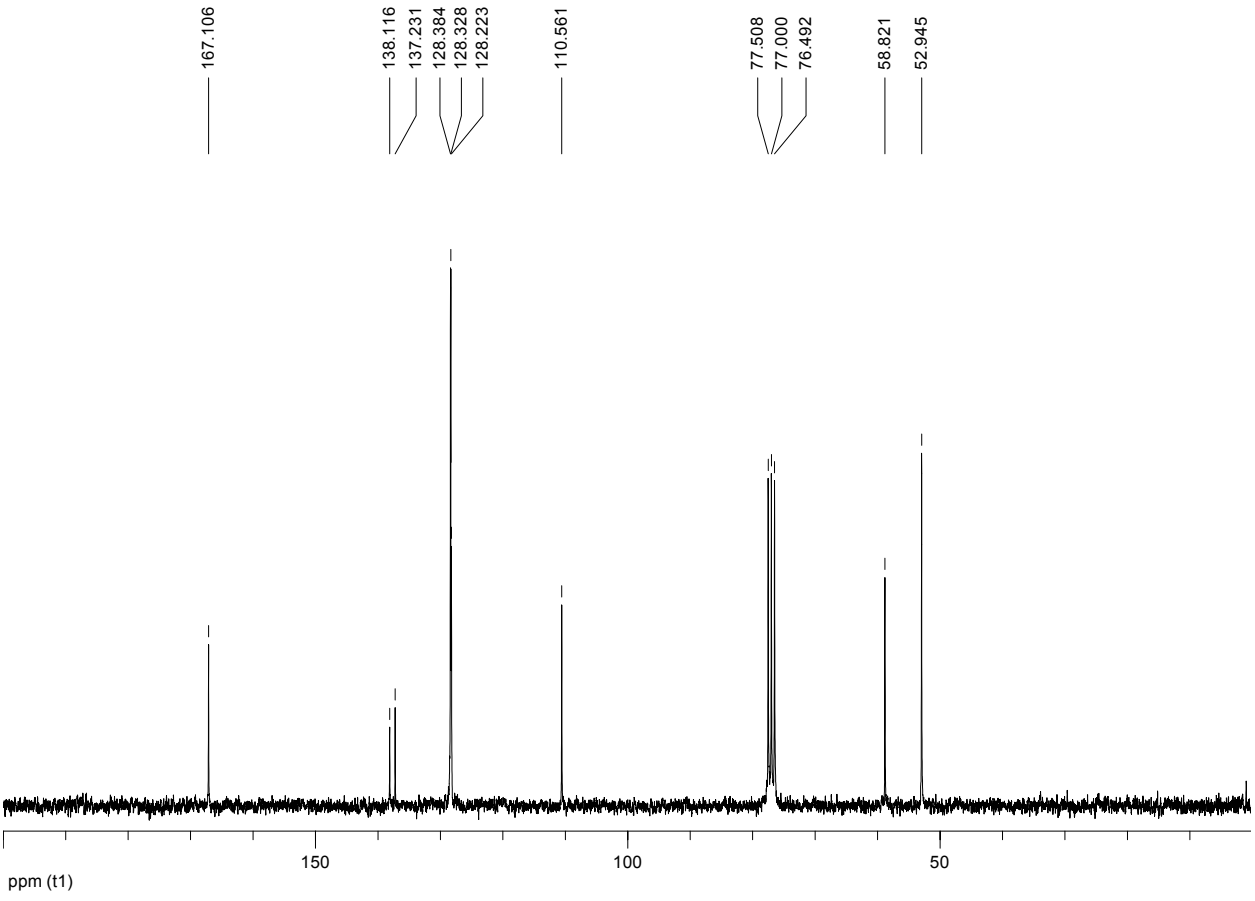


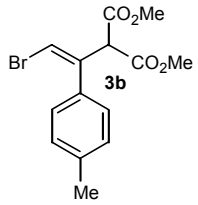
3a

^{1}H NMR (360 MHz, $CDCl_3$)



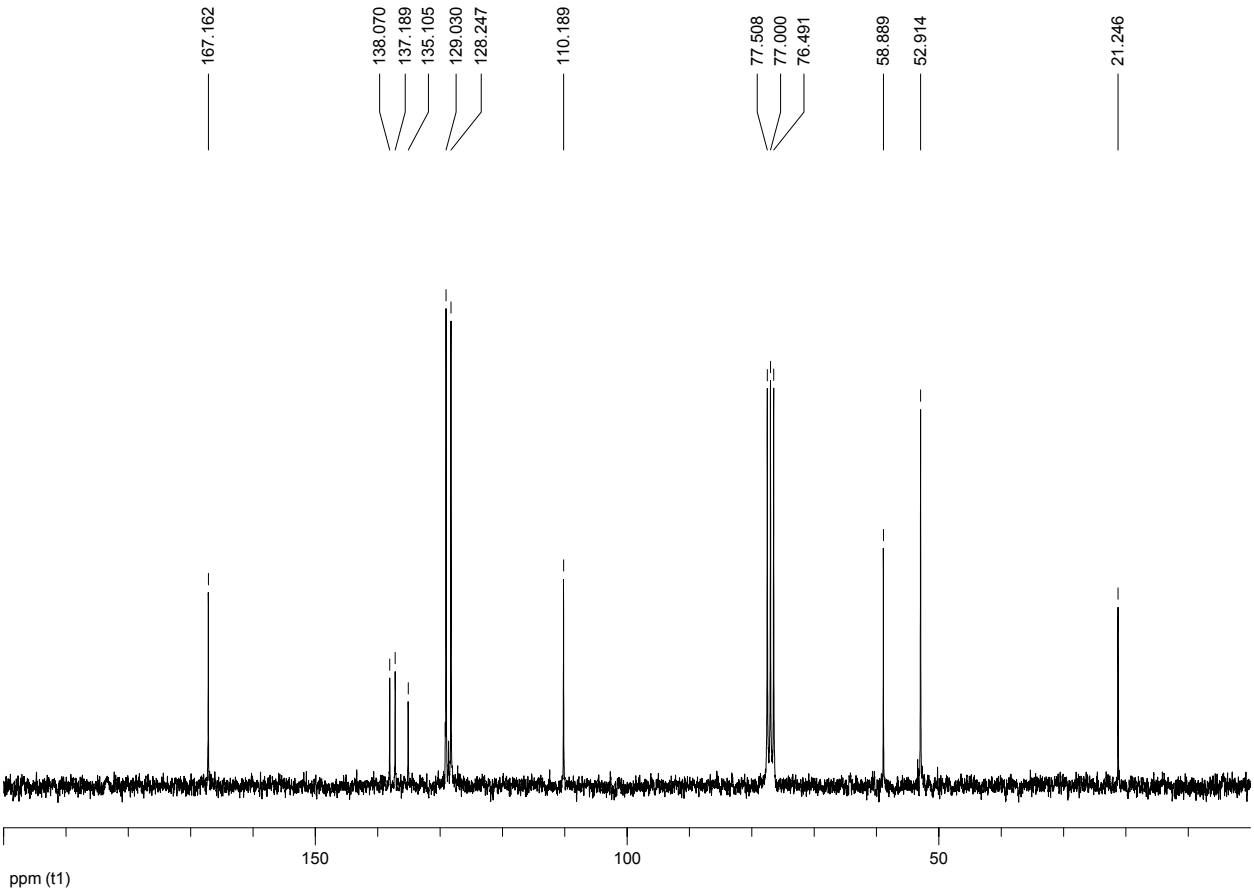
^{13}C NMR (62.9 MHz, $CDCl_3$)

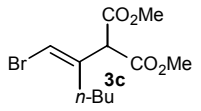




^{1}H NMR (360 MHz, $CDCl_3$)

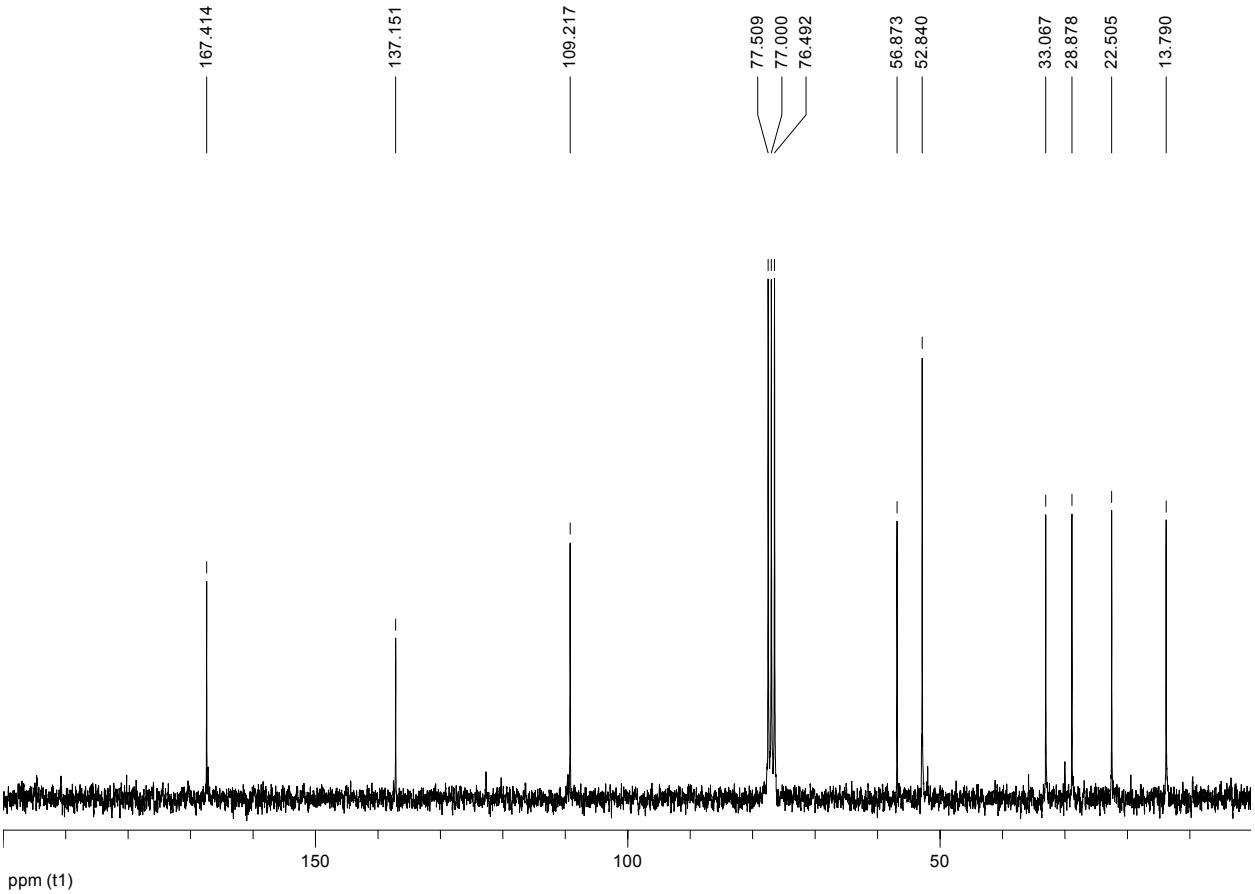
^{13}C NMR (62.9 MHz, $CDCl_3$)

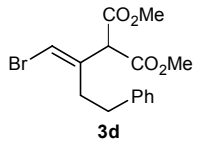




^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)

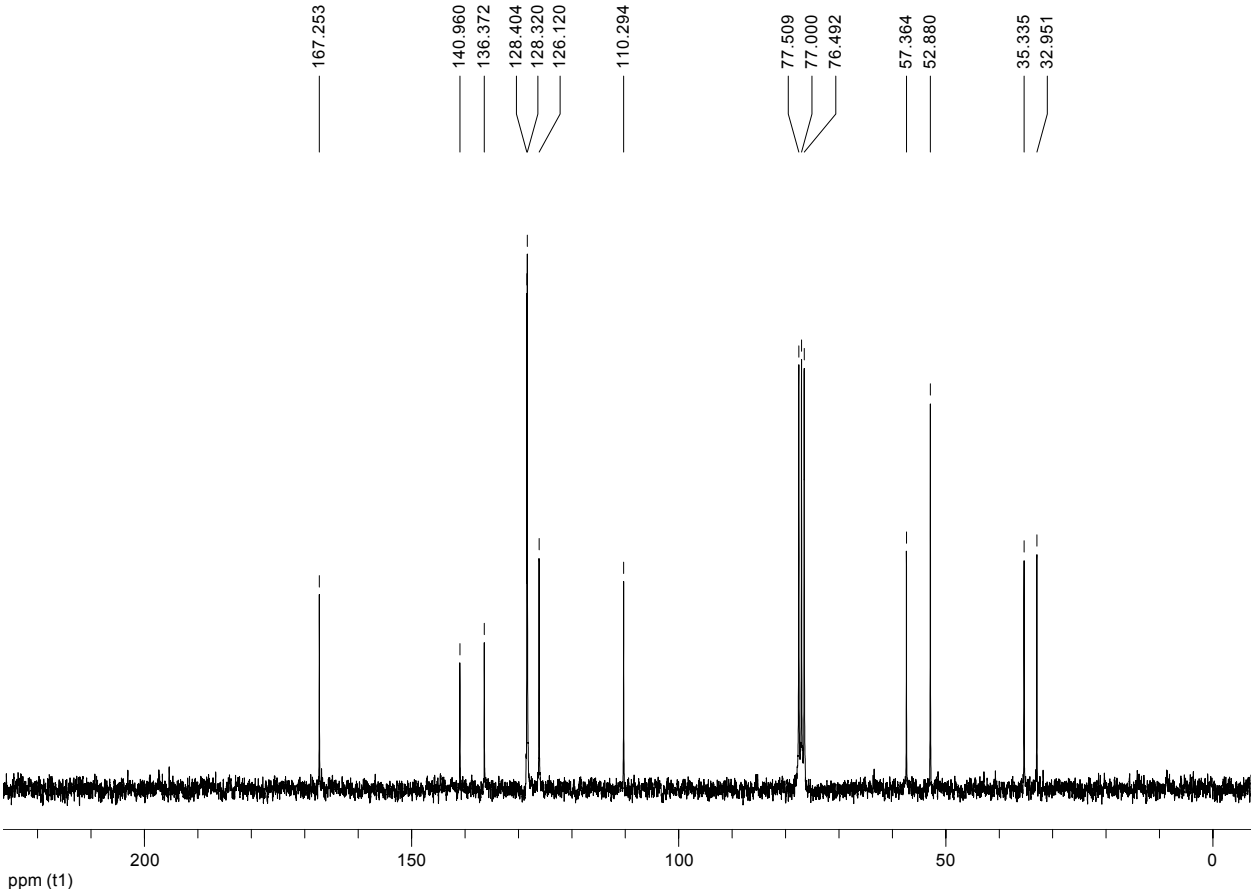


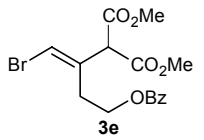


3d

^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)

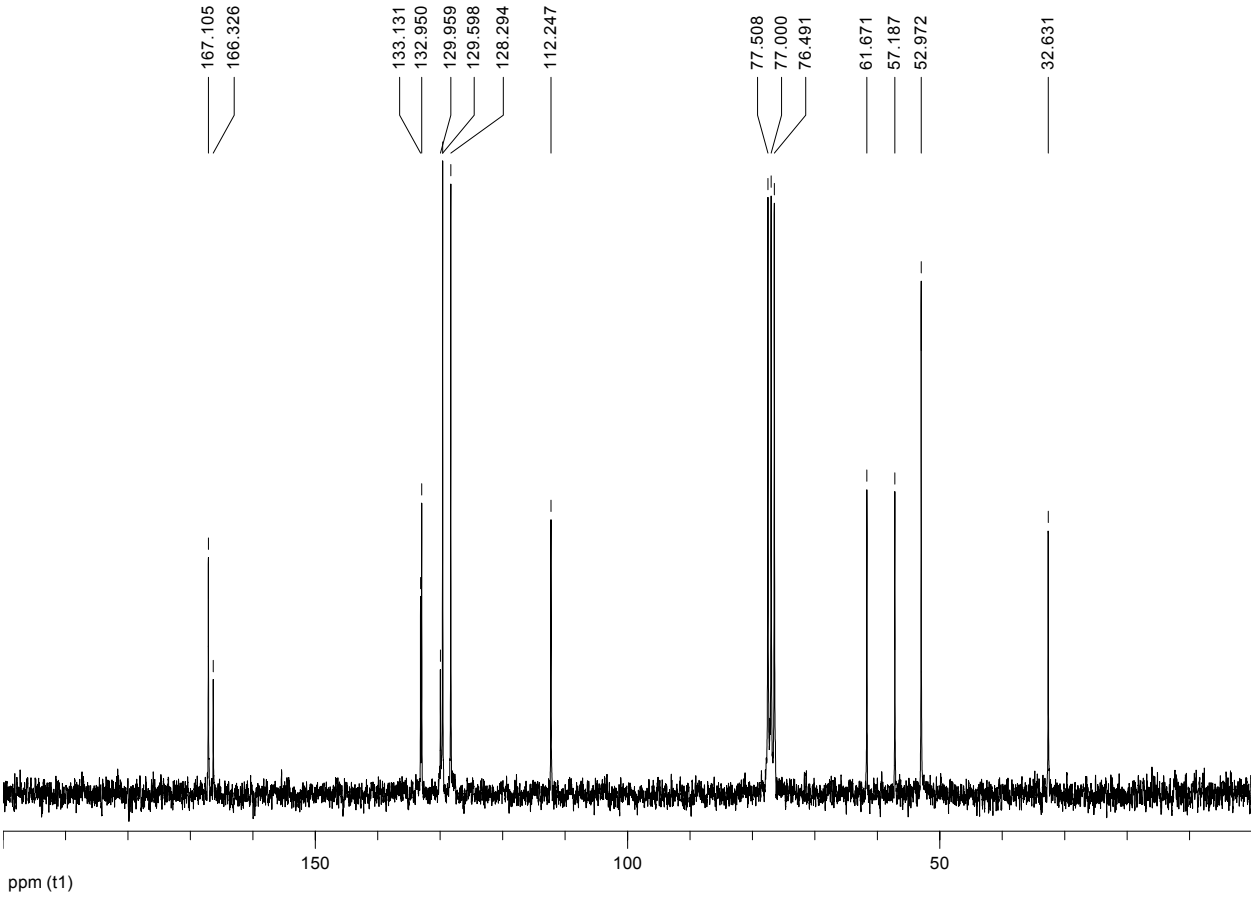


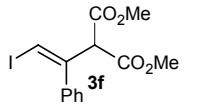


3e

^{1}H NMR (360 MHz, $CDCl_3$)

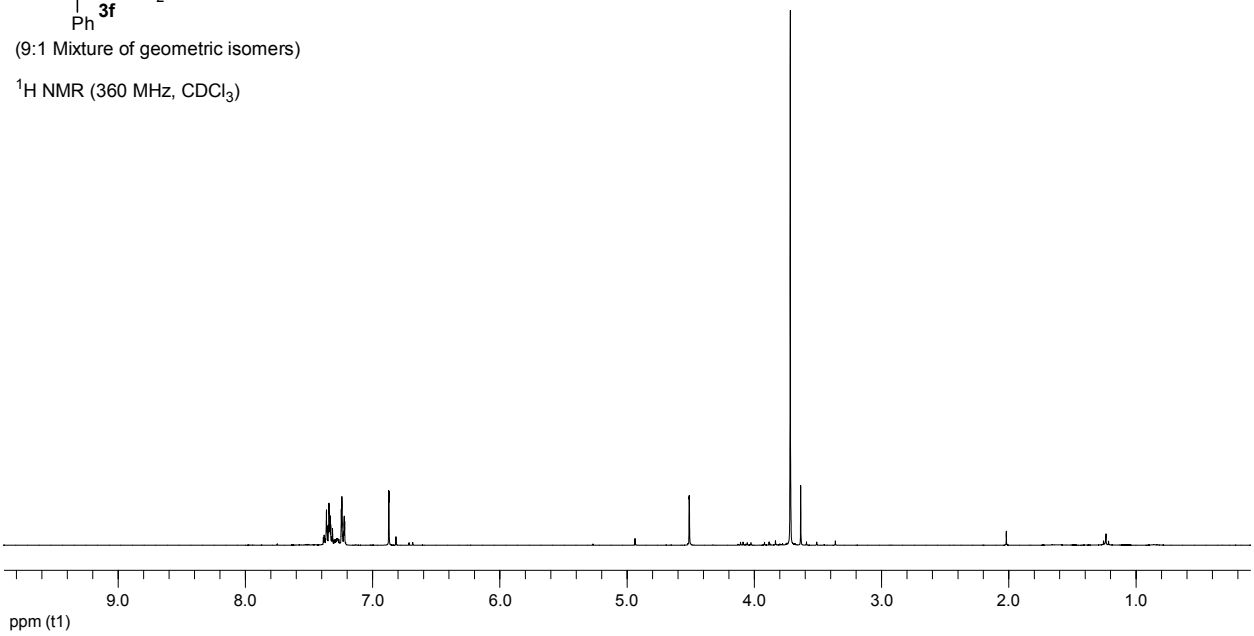
^{13}C NMR (62.9 MHz, $CDCl_3$)



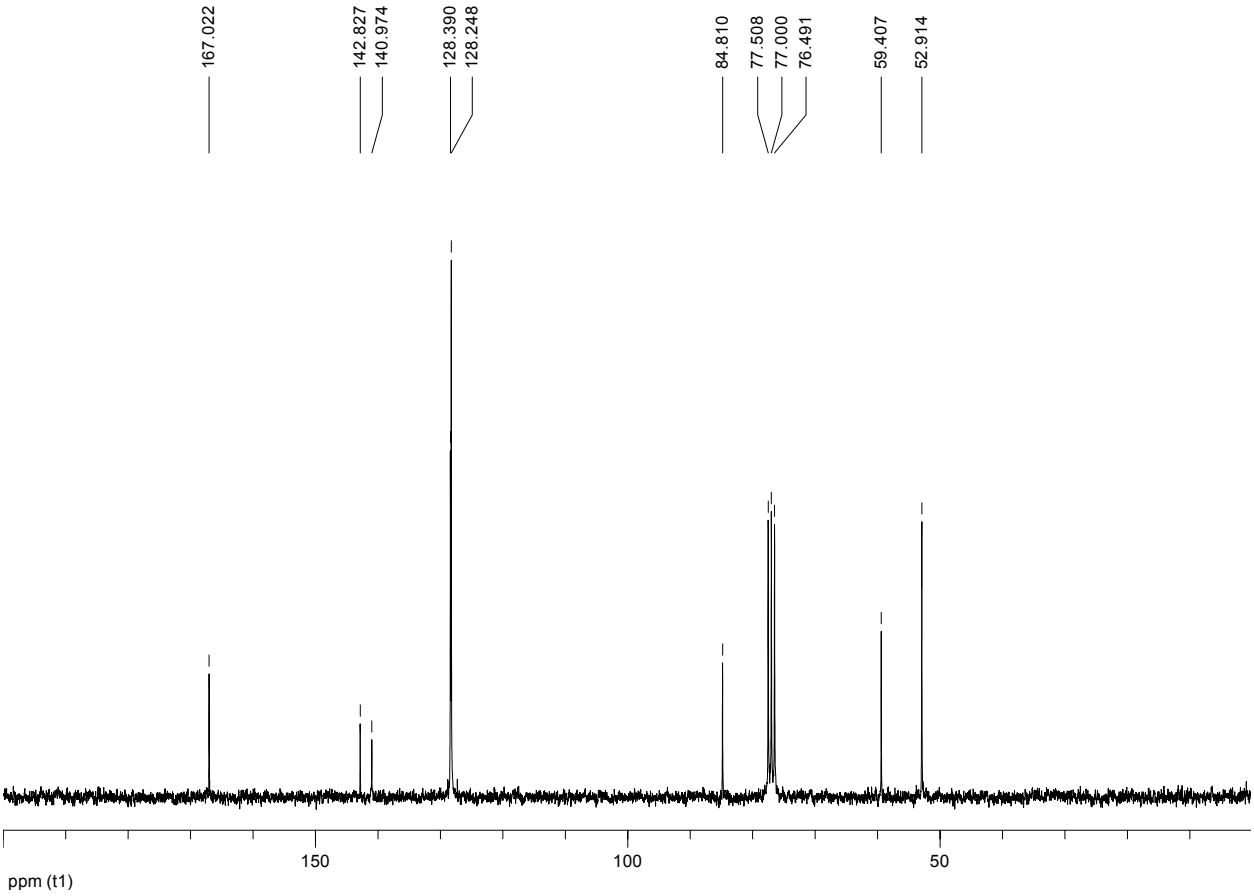


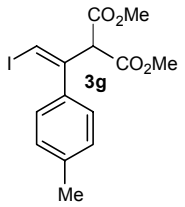
(9:1 Mixture of geometric isomers)

^{1}H NMR (360 MHz, $CDCl_3$)

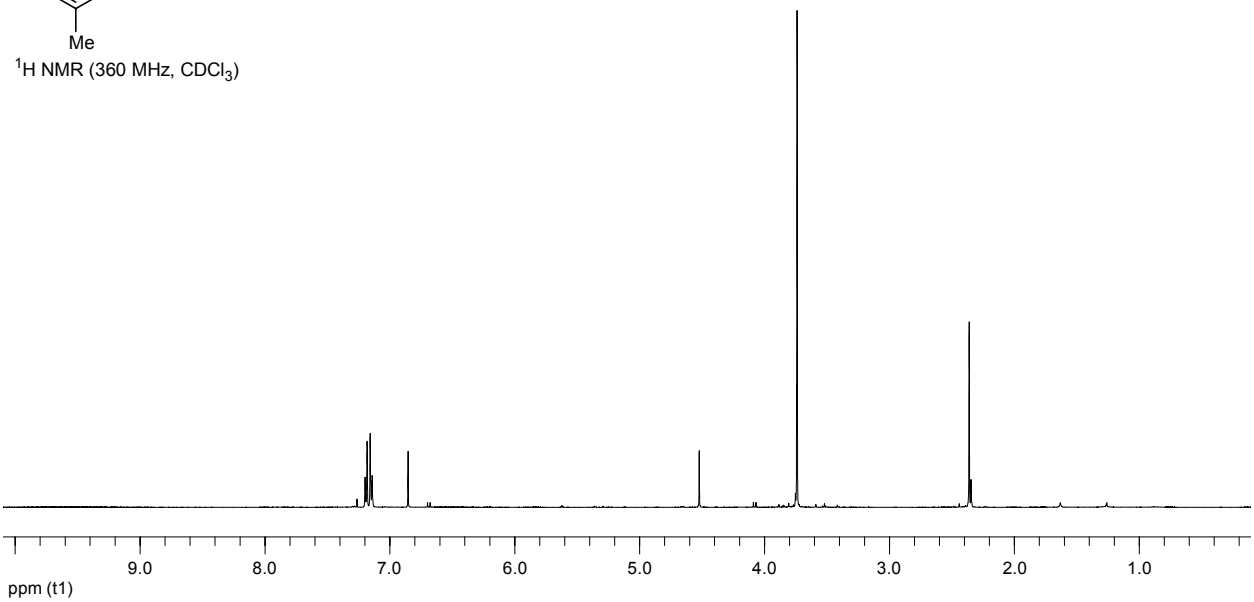


^{13}C NMR (62.9 MHz, $CDCl_3$)

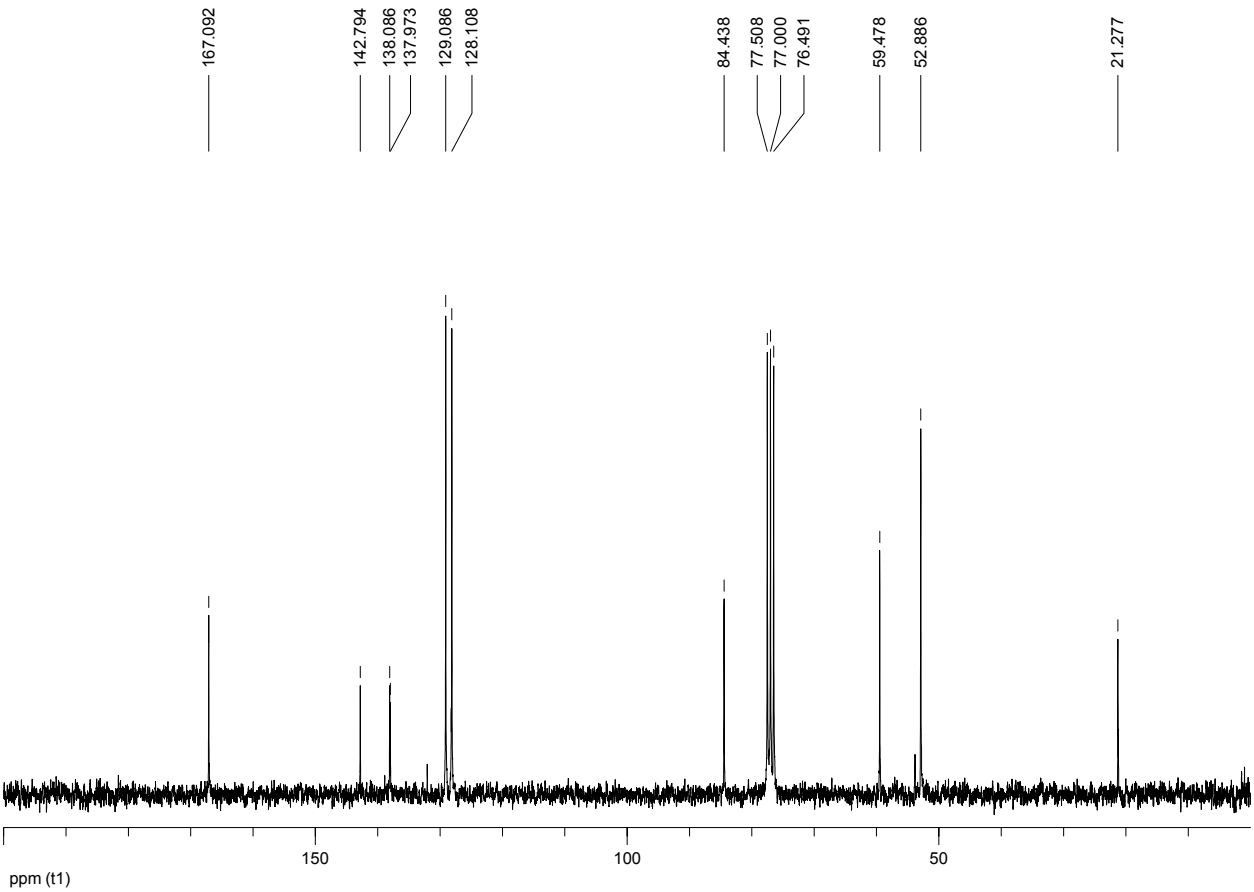


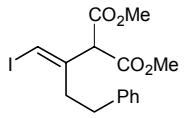


^{1}H NMR (360 MHz, $CDCl_3$)



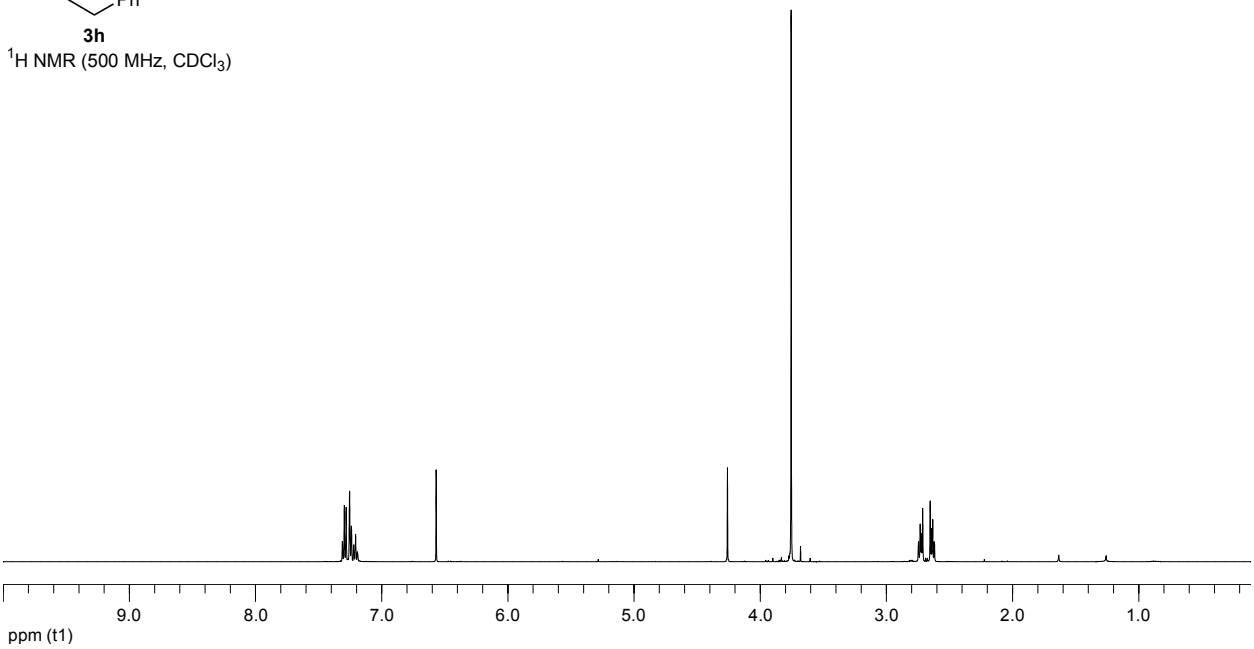
^{13}C NMR (62.9 MHz, $CDCl_3$)



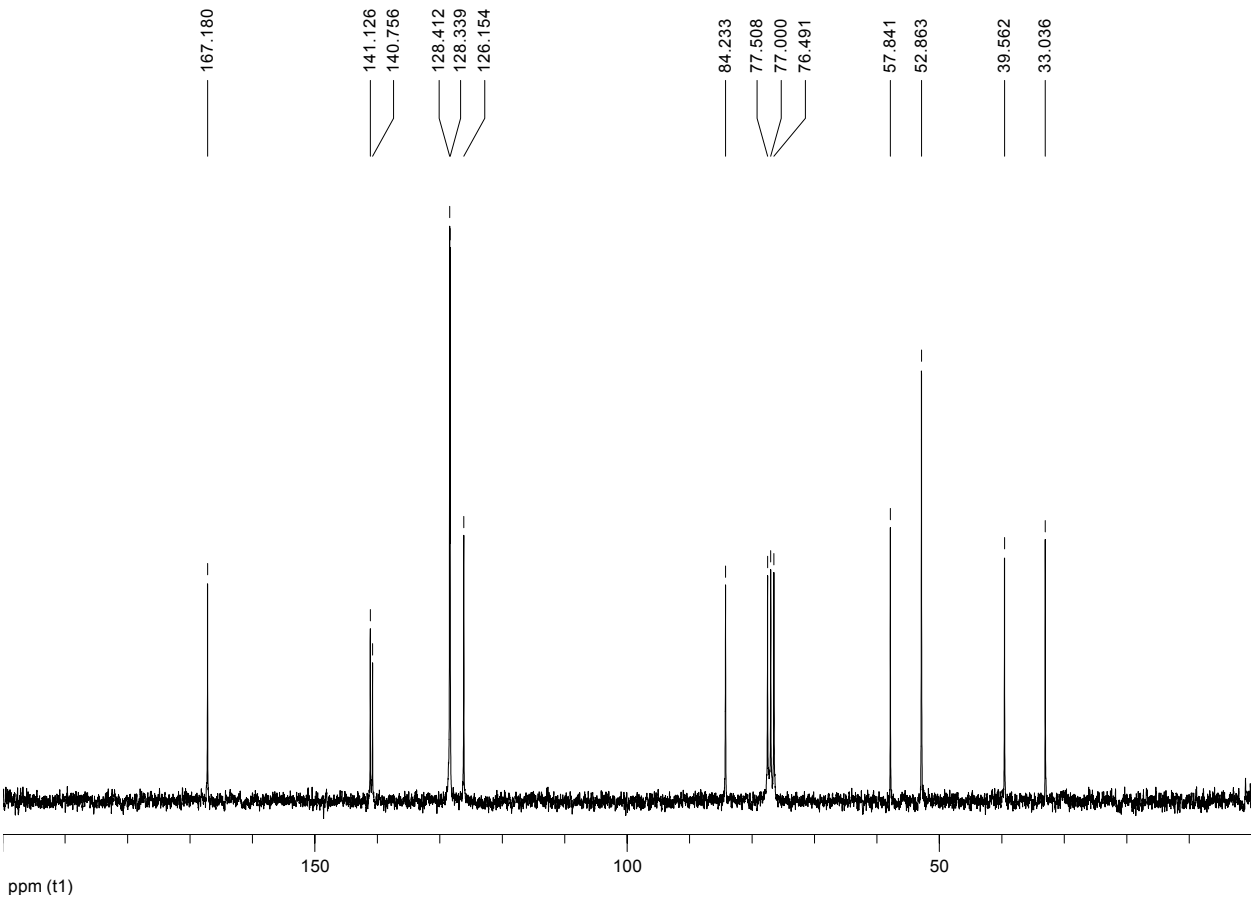


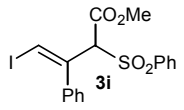
3h

^{1}H NMR (500 MHz, $CDCl_3$)



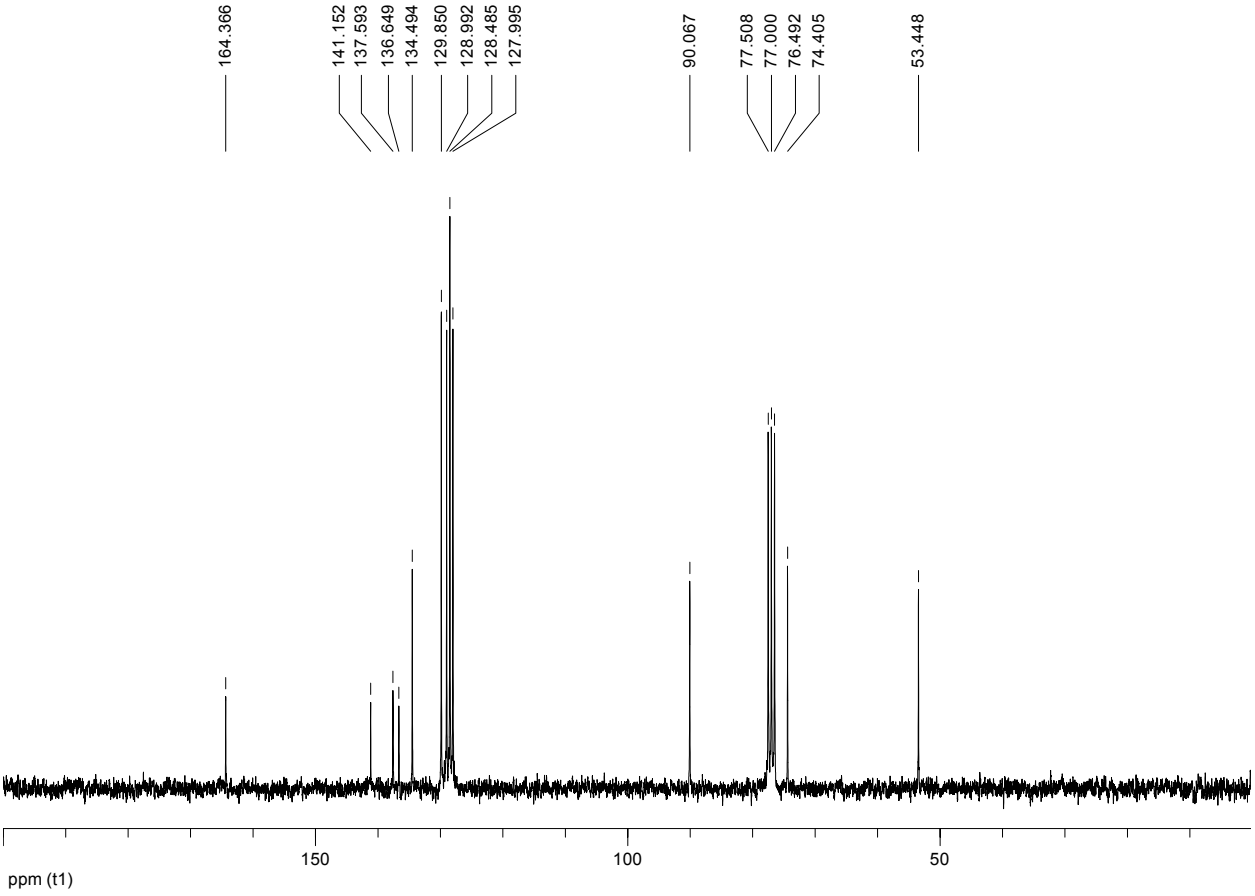
^{13}C NMR (62.9 MHz, $CDCl_3$)

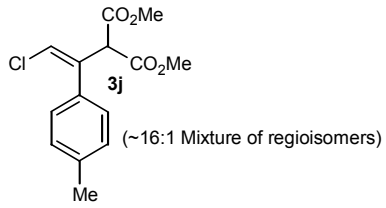




^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)

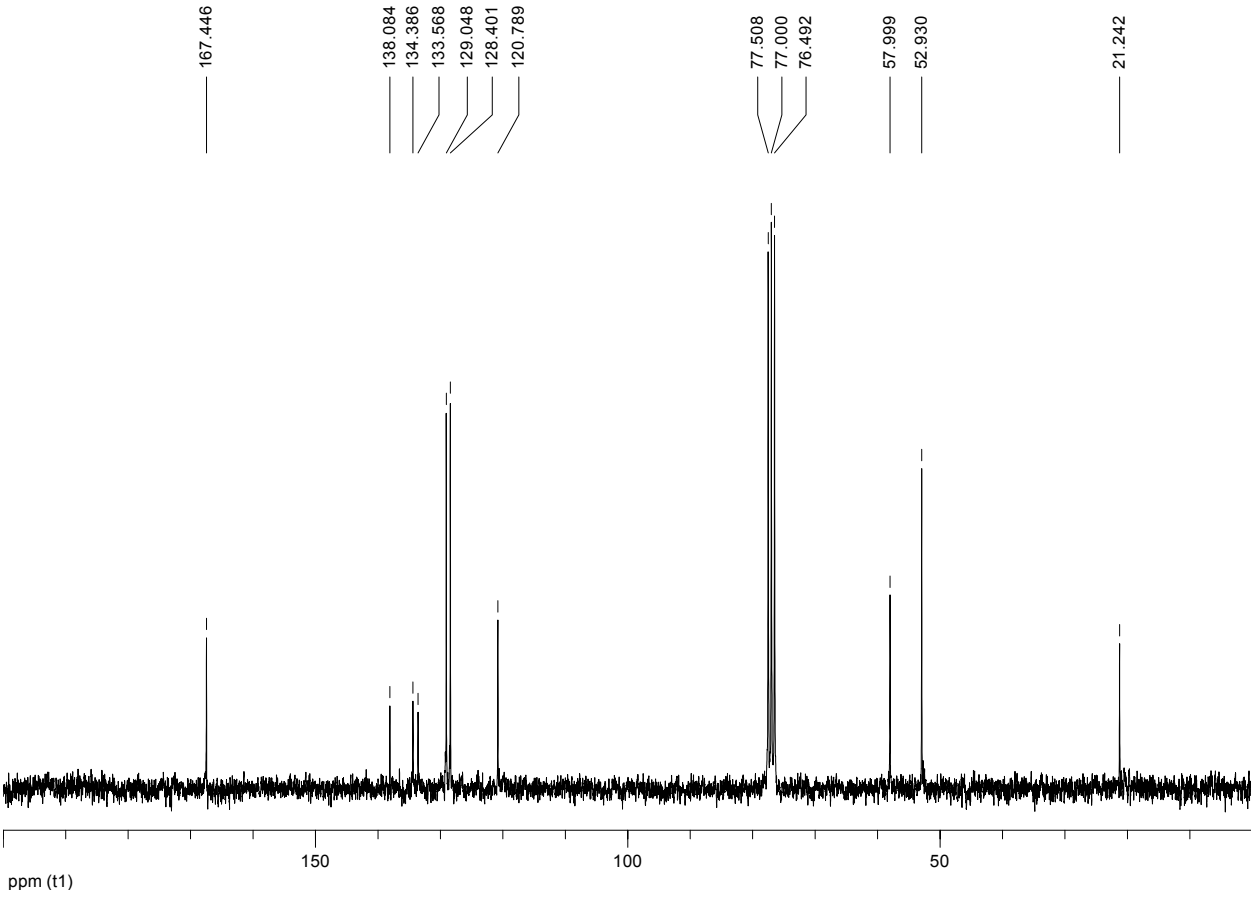


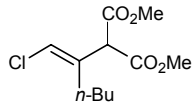


(~16:1 Mixture of regioisomers)

^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)



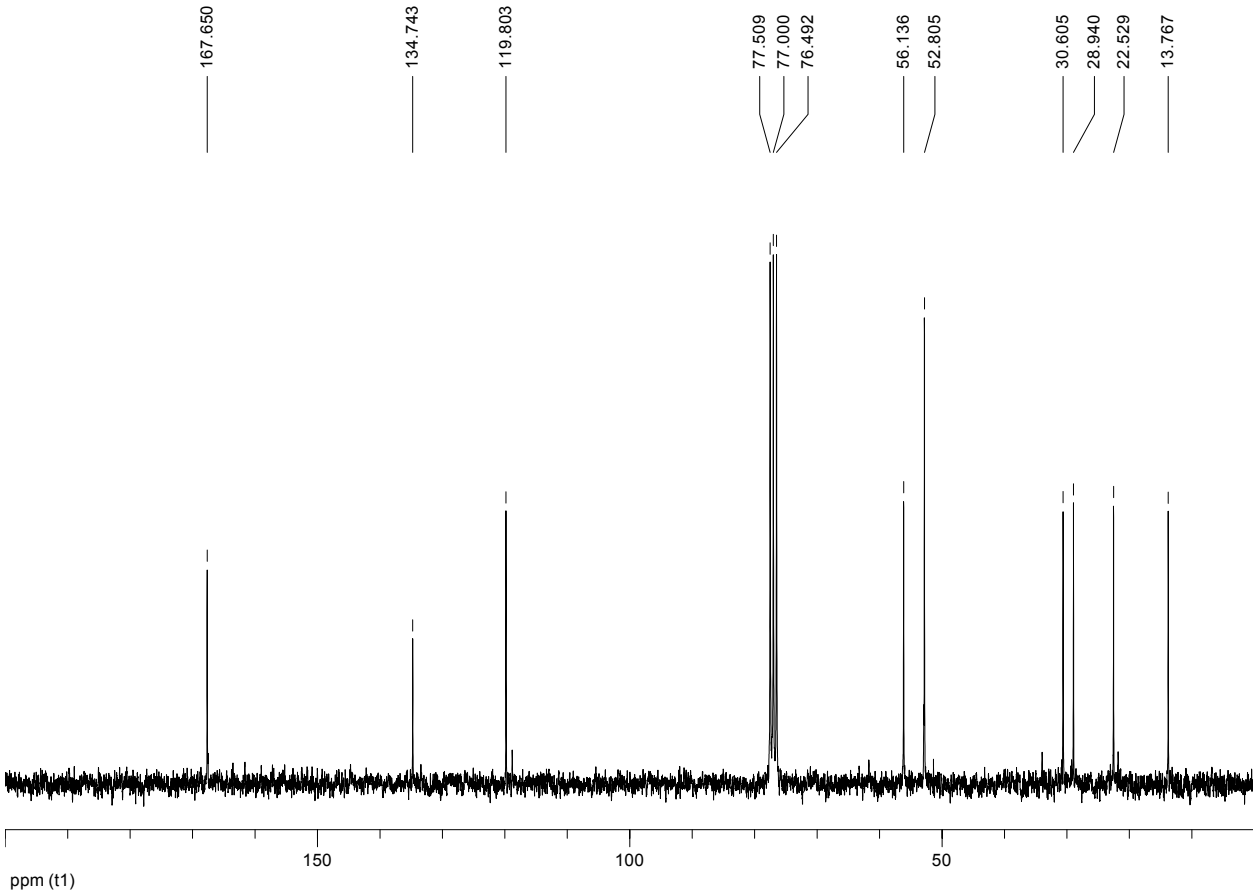


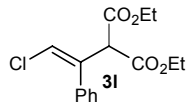
3k

(~16:1 Mixture of regioisomers)

^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)

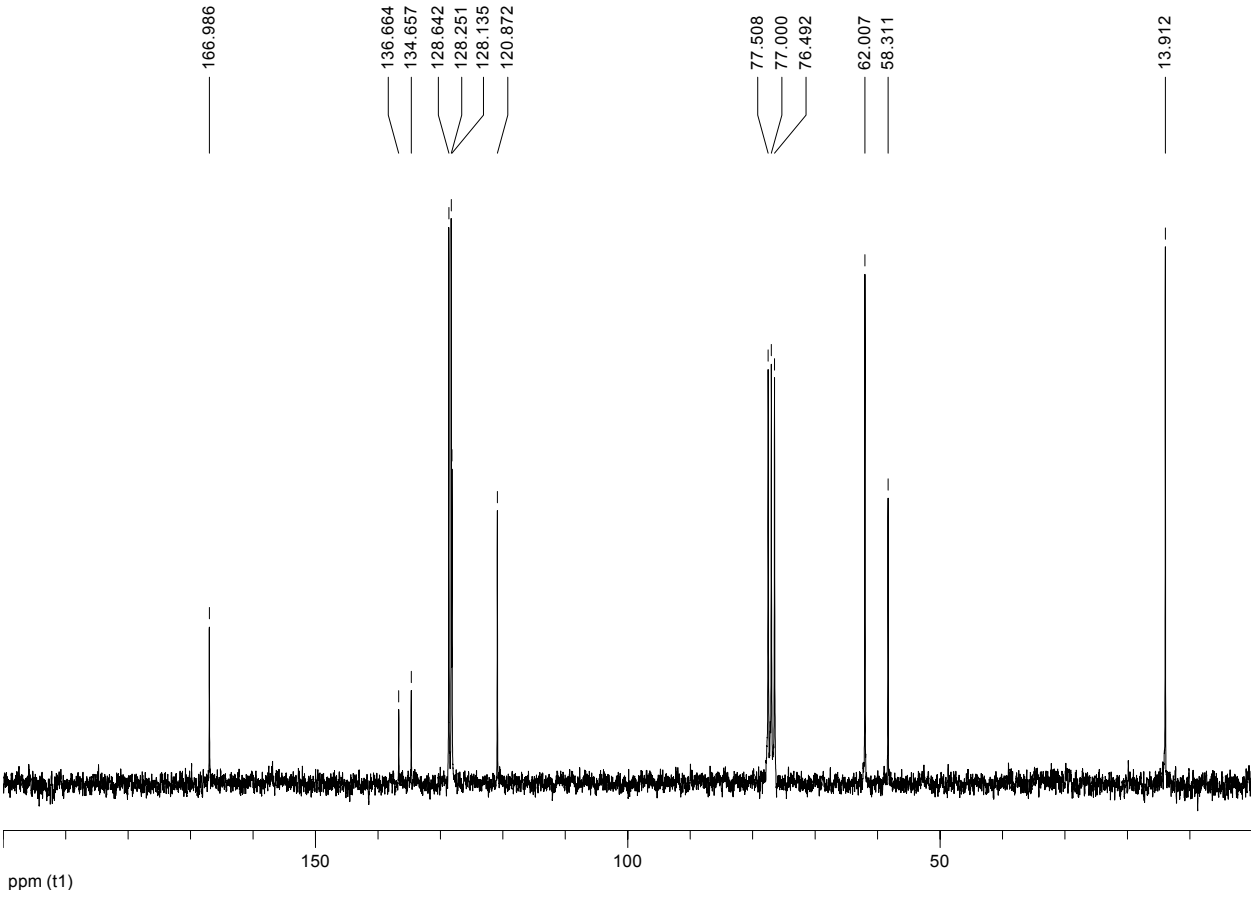


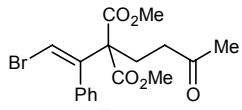


3l

^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)

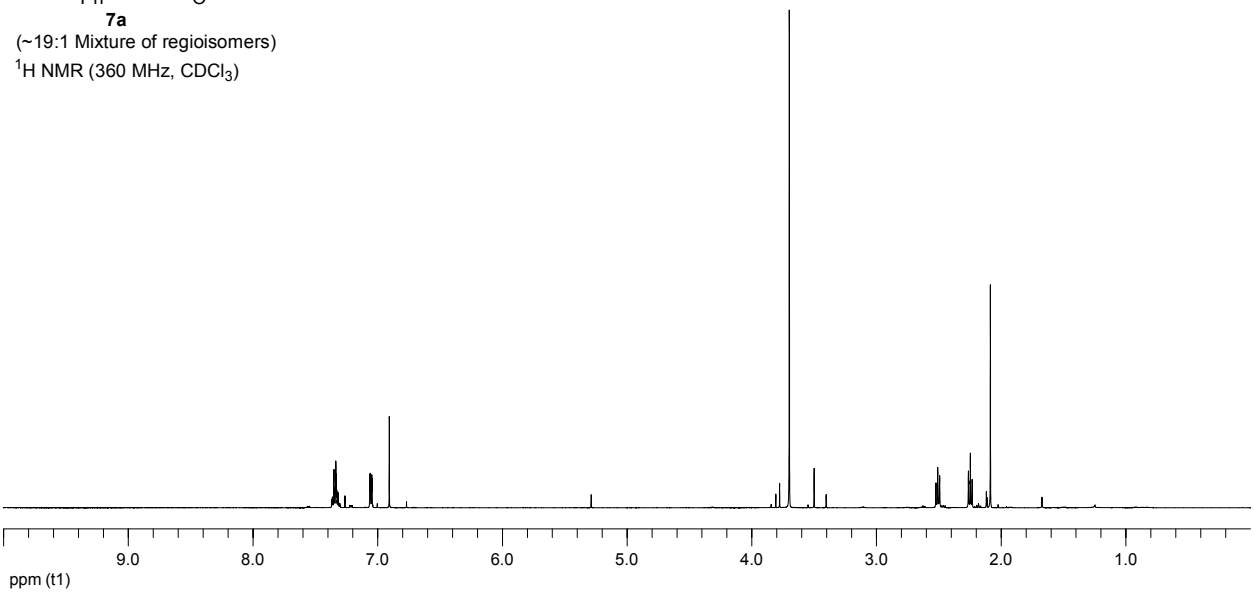




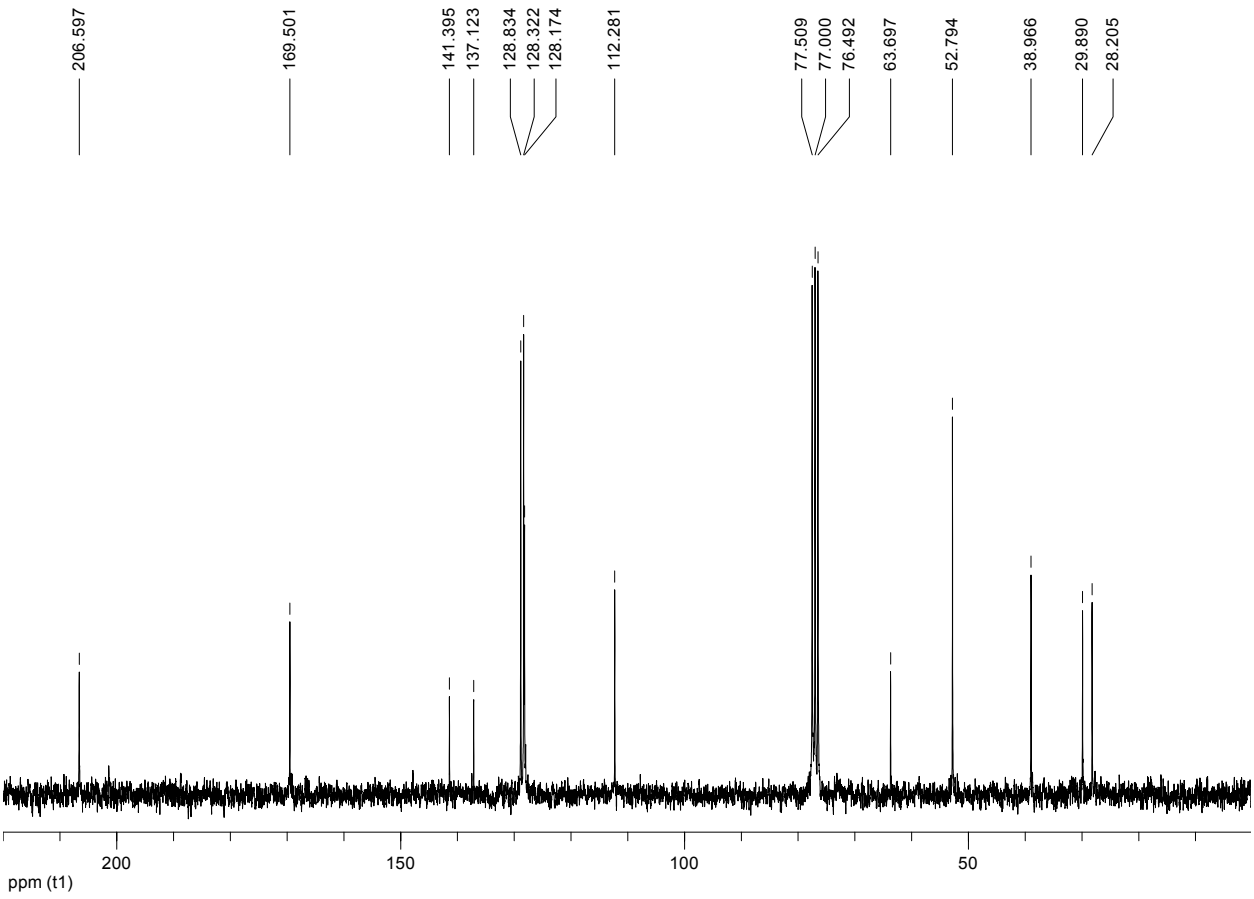
7a

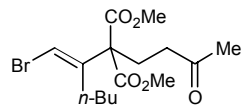
(~19:1 Mixture of regioisomers)

^{1}H NMR (360 MHz, $CDCl_3$)



^{13}C NMR (62.9 MHz, $CDCl_3$)

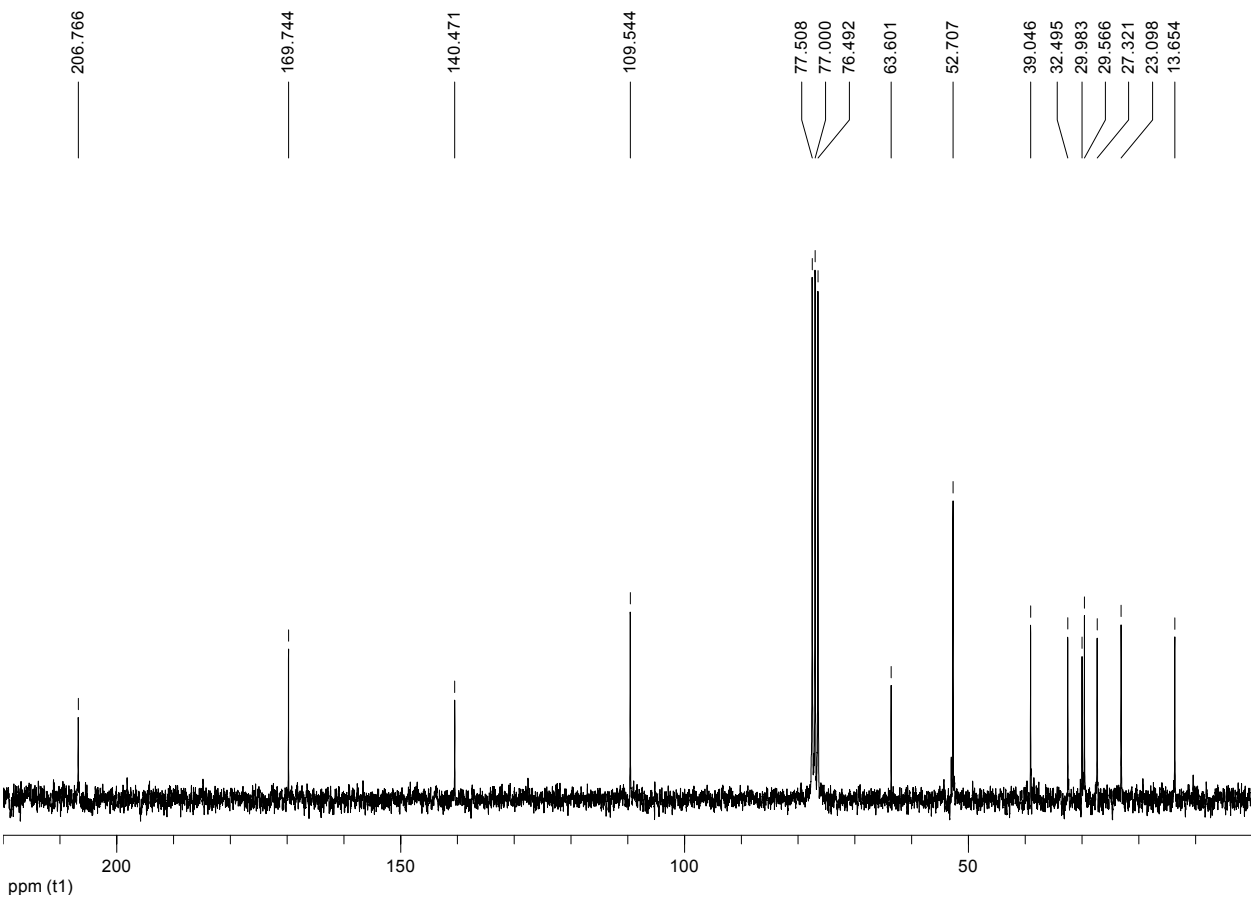


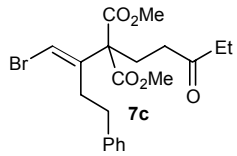


7b

^{1}H NMR (360 MHz, $CDCl_3$)

^{13}C NMR (62.9 MHz, $CDCl_3$)





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