SUPPORTING INFORMATION

Functionalization of primary carbon-hydrogen bonds of alkanes by carbene insertion with a silver-based catalyst

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Catalytic Experiments.

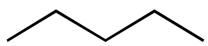
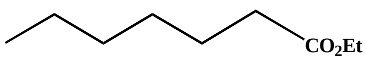
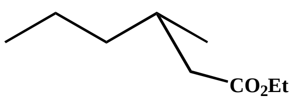
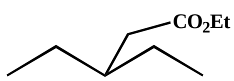
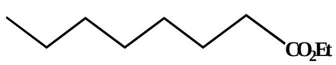
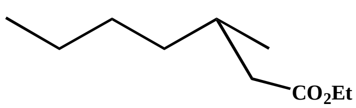
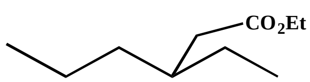
Complex **1** (20 mg, 0.019 mmol) was suspended in 5 mL of the corresponding substrate and 0.75 mmol of EDA were added in one portion to the stirred mixture. The flask was covered with aluminium foil to avoid exposure to light. After 2-5 h of stirring, depending of the substrate, no EDA was detected by GC.

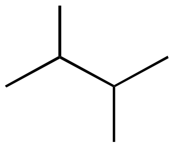
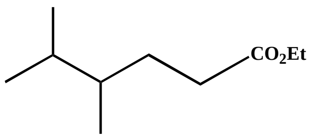
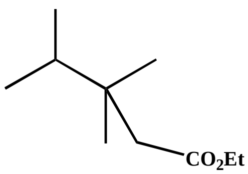
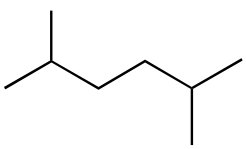
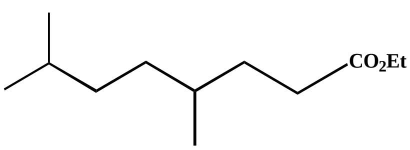
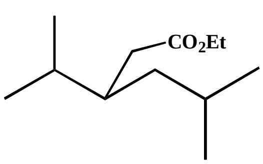
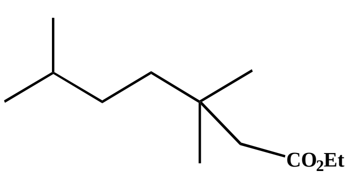
Reported yields correspond to, at least, average of two runs, and were determined in the following manner. After removal of volatiles (at 0 ºC to avoid loss of low boiling point compounds), the crude product was investigated by ^{1}H NMR spectroscopy, with a standard being added (tosyl chloride, styrene) to ensure that all the initial EDA was converted in the observed products. The observed ratios were compared to those from GC analysis at the end of the reaction, in order to establish the response factors. The subsequent experiments were then checked by GC using such factors.

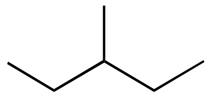
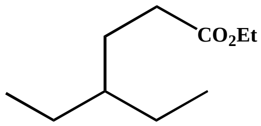
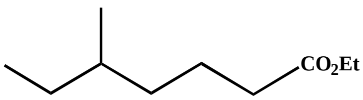
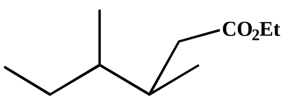
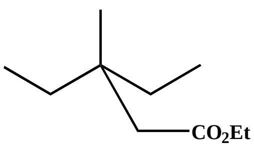
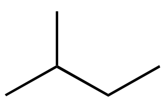
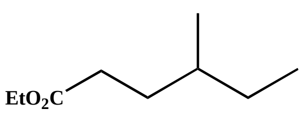
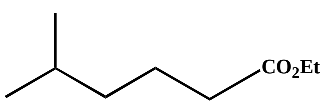
The products were characterized by NMR and GC-MS. The representative resonances (NMR) and fragmentations (GCMS) are shown in the following pages.

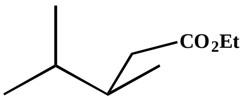
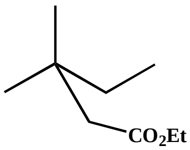
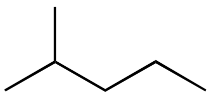
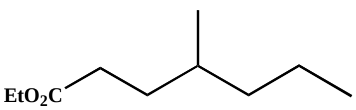
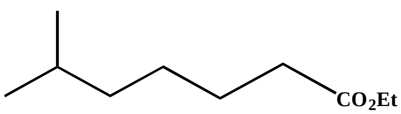
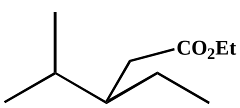
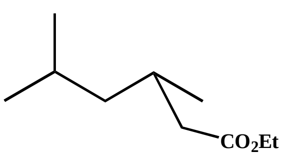
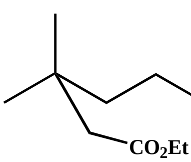
Spectroscopic data for products obtained from the reaction of alkanes and EDA in the presence of 1.

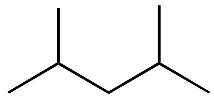
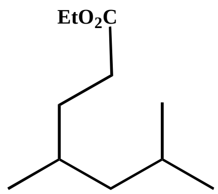
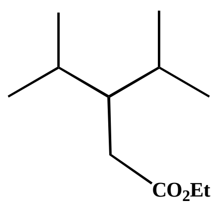
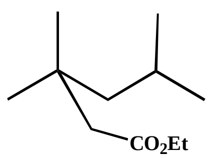
Table 1. Selected *NMR* data: (400 MHz, 20 °C, $CDCl_3$)

Substrate 1 	**^{1}H NMR (ppm)** **RCH_2CO_2Et** (*H* italic)	**^{13}C{^{1}H} NMR(ppm)** **RCH_2CO_2Et** (*C* italic)
Product 1a 	2.25 (t, 2H J= 7.5 Hz)	34.7
Product 1b 	2.28 (dd, 1H, J= 14.5, 6 Hz) 2.08 (dd, 1H, J= 14.5, 8.1 Hz)	42.2
Product 1c 	2.22 (d, 2H, J= 6.9 Hz)	39.3
Substrate 2 	**^{1}H NMR (ppm)** **RCH_2CO_2Et**	**^{13}C{^{1}H} NMR(ppm)** **RCH_2CO_2Et**
Product 2a 	2.27 (t, 2H, J= 7.5 Hz)	34.6
Product 2b 	2.28 (dd, 1H, J= 14.5, 6.2 Hz) 2.08 (dd, 1H, J= 14.5, 8.1 Hz)	42.1
Product 2c 	2.22 (d, 2H, J= 6.9 Hz)	39.1

Substrate 3 	**^{1}H NMR (ppm)** **$RC\mathit{H}_2CO_2Et$**	**$^{13}C\{^{1}H\}$ NMR(ppm)** **$R\mathit{C}H_2CO_2Et$**
Product 3a 	2.25 (m, 2H)	33.0
Product 3b 	2.20 (s, 2H)	44.8
Substrate 4 	**^{1}H NMR (ppm)** **$RC\mathit{H}_2CO_2Et$**	**$^{13}C\{^{1}H\}$ NMR(ppm)** **$R\mathit{C}H_2CO_2Et$**
Product 4a 	2.25 (m, 2H)	32.5
Product 4b 	2.20 (dd, 1H, J= 15, 6.8 Hz) 2.07 (dd, 1H, J= 15, 7.2 Hz)	36.7
Product 4c 	2.14 (s, 2H)	46.3

Substrate 5 	**^{1}H NMR (ppm)** **RC*H*$_2$CO$_2$Et**	**^{13}C{^{1}H} NMR(ppm)** **R*C*H$_2$CO$_2$Et**
Product 5a 	2.25 (m, 2H)	35.0
Product 5b 	2.29 (m, 2H)	38.5
Product 5c 	2.26 (dd, 1H, J= 4.3, 5.2 Hz) 2.07 (dd, 1H, J= 14.3, 8.7 Hz)	40.3
Product 5d 	2.15 (s, 2H)	43.5
Substrate 6 	**^{1}H NMR (ppm)** **RC*H*$_2$CO$_2$Et**	**^{13}C{^{1}H} NMR(ppm)** **R*C*H$_2$CO$_2$Et**
Product 6a 	2.29 (m, 2H)	32.5
Product 6b 	2.25 (m. 2H)	35.0

Product 6c 	2.30 (dd, 1H, J= 14.6, 5.2 Hz) 2.05 (dd, 1H, J= 14.6, 9.2 Hz)	38.7
Product 6d 	2.16 (s, 2H)	46.0
Substrate 7 	**^{1}H NMR (ppm)** **RCH_2CO$_2$Et**	**^{13}C{^{1}H} NMR(ppm)** **R*C*H$_2$CO$_2$Et**
Product 7a 	2.28 (m. 2H)	32.3
Product 7b 	2.28 (t, 2H, J= 7.5 Hz)	34.6
Product 7c 	nd	nd
Product 7d 	2.28 (dd, 1H, J= 14.1, 5.1 Hz) 2.08 (dd, 1H, J= 4.1, 8.1 Hz)	42.5
Product 7e 	2.16 (s, 2H)	46.5

Substrate 8 	**[1]H NMR (ppm)** **RC*H*$_2$CO$_2$Et**	**[13]C{[1]H} NMR(ppm)** **R*C*H$_2$CO$_2$Et**
Product 8a 	2.29 (m, 2H)	32.3
Product 8b 	2.16 (d, 2H, J= 5.6 Hz)	33.3
Product 8c 	2.20 (s, 2H)	47.0

Mass Spectrometry data for products

GC/MS for 1a: m/z (relative intensity): 159 [M^+], 143 [$M-CH_3^+$], 129 [$M-CH_2-CH_3^+$], 113 [$M-OCH_2-CH_3^+$], 101 [$CH_2-CH_2CO_2Et$], 73 [$M-CO_2Et$], 70, 61.

GC/MS for 1b: m/z (relative intensity): 159 [M^+], 143 [$M-CH_3^+$], 129 [$M-CH_2-CH_3^+$], 115 [$M-CH_2-CH_2-CH_3$], 88 [CH_2CO_2Et],70, 61.

GC/MS for 1c: m/z (relative intensity): 159 [M^+], 143 [$M-CH_3^+$], 129 [$M-CH_2-CH_3^+$], 115 [$M-CH_2-CH_2-CH_3$], 88 [CH_2CO_2Et],70, 61.

GC/MS for 2a: m/z (relative intensity): 173 [M^+], 157 [$M-CH_3^+$], 143 [$M-CH_2-CH_3^+$], 127 [$M-OCH_2-CH_3^+$], 115, 101 [$CH_2-CH_2CO_2Et$], 73 [$M-CO_2Et$], 70, 61, 57.

GC/MS for 2b: m/z (relative intensity): 173 [M^+], 157 [$M-CH_3^+$], 143 [$M-CH_2-CH_3^+$], 127 [$M-OCH_2-CH_3^+$], 115, 73 [$M-CO_2Et$], 88 [$CH_2CO_2Et^+$], 70, 61, 57.

GC/MS for 2c: m/z (relative intensity): 173 [M^+], 157 [$M-CH_3^+$], 143 [$M-CH_2-CH_3^+$], 127 [$M-OCH_2-CH_3^+$], 115, 73 [$M-CO_2Et$], 88 [$CH_2CO_2Et^+$],70, 61, 57.

GC/MS for 3a: m/z (relative intensity): 173 [M^+], 157 [$M-CH_3^+$], 127 [$M-OCH_2-CH_3^+$], 115, 101 [$CH_2-CH_2CO_2Et$], 73 [$M-CO_2Et$], 55.

GC/MS for 3b: m/z (relative intensity): 173 [M^+], 157 [$M-CH_3^+$], 127 [$M-OCH_2-CH_3^+$], 115, 87 [$M-CH_2CO_2Et$], 88, 73 [$M-CO_2Et$], 69, 55.

GC/MS for 4a: m/z (relative intensity): 201 [M^+], 185 [$M-CH_3^+$], 157 [$M-C(CH_3)_2^+$], 129, 111 [$M-CH_2-CH_2CO_2Et$], 101 [$CH_2-CH_2CO_2Et$], 73, 71.

GC/MS for 4b: m/z (relative intensity): 201 [M^+], 185 [$M-CH_3^+$], 157 [$M-C(CH_3)_2^+$], 129, 111 [$M-CH_2-CH_2CO_2Et$], 88, 71.

GC/MS for 4c: m/z (relative intensity): 201 [M^+], 185 [$M-CH_3^+$], 157 [$M-C(CH_3)_2^+$], 129, 111 [$M-CH_2-CH_2CO_2Et$], 88, 71.

GC/MS for 5a: m/z (relative intensity): 159 [M^+], 143 [$M-CH_3^+$], 129 [$M-CH_2-CH_3^+$], 113 [$M-OCH_2-CH_3^+$], 101 [$CH_2-CH_2CO_2Et$], 88, 73 [$M-CO_2Et$].

GC/MS for 5b: m/z (relative intensity): 159 [M^+], 143 [$M-CH_3^+$], 129 [$M-CH_2-CH_3^+$], 113 [$M-OCH_2-CH_3^+$], 101 [$CH_2-CH_2CO_2Et$], 88, 73 [$M-CO_2Et$].

GC/MS for 5c: m/z (relative intensity): 159 [M^+], 143 [M-CH_3^+], 129 [M-CH_2-CH_3^+], 113 [M-OCH_2-CH_3^+], 88, 71.
GC/MS for 5d: m/z (relative intensity): 159 [M^+], 143 [M-CH_3^+], 129 [M-CH_2-CH_3^+], 113 [M-OCH_2-CH_3^+], 88, 71.

GC/MS for 6a and 6b: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 129, 115, 109, 101 [CH_2-CH_2CO_2Et], 73 [M-CO_2Et], 69, 61
GC/MS for 6c: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 115, 109, 88 [CH_2CO_2Et], 73 [M-CO_2Et], 69, 61.
GC/MS for 6d: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 115, 109, 88 [$CH_2CO_2Et^+$], 73 [M-CO_2Et], 69, 61.

GC/MS for 7a and 7b: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 129 [M-CH_2-CH_2-$CH3^+$], 115, 109, 101 [CH_2-CH_2CO_2Et], 88, 73 [M-CO_2Et], 61
GC/MS for 7c and 7d: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 88 [$CH_2CO_2Et^+$], 85, 73, 69, 61.
GC/MS for 7e: m/z (relative intensity): 173 [M^+], 157 [M-CH_3^+], 143 [M-CH_2-CH_3^+], 88 [$CH_2CO_2Et^+$], 85, 73, 69, 61.

GC/MS for 8a: m/z (relative intensity): 187 [M^+], 171 [M-CH_3^+], 143 [M-CH-$(CH_3)_2^+$], 129[M-CH_2-CH-$(CH_3)_2^+$], 123, 101 [CH_2-CH_2CO_2Et], 88, 73 [M-CO_2Et],55.
GC/MS for 8b and 8c: m/z (relative intensity): 187 [M^+], 171 [M-CH_3^+], 143 [M-CH-$(CH_3)_2^+$], 129 [M-CH_2-CH-$(CH_3)_2^+$], 88 [$CH_2CO_2Et^+$] ,57.